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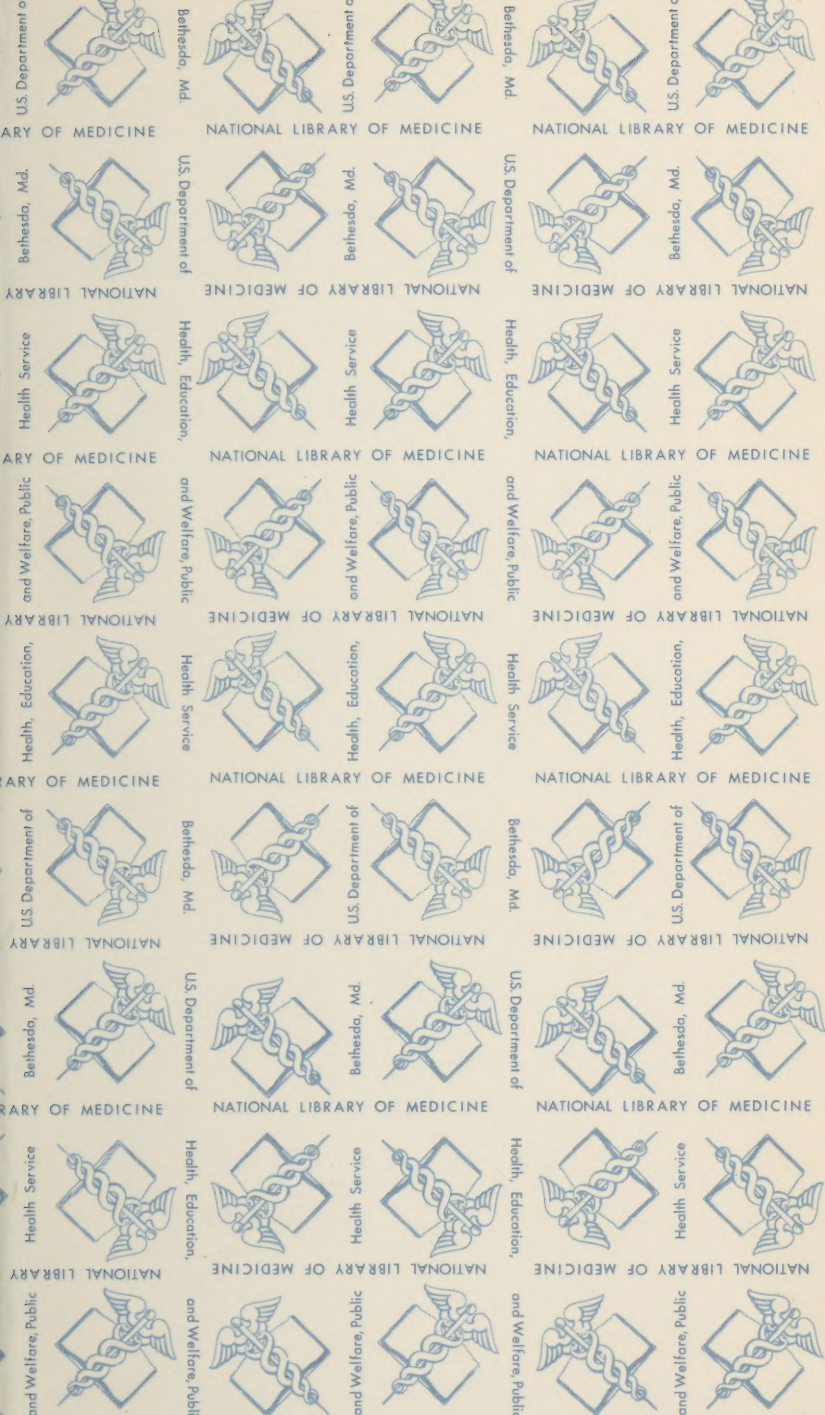
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AN ELEMENTARY TREATISE

ON

147

# PRACTICAL CHEMISTRY

AND

QUALITATIVE INORGANIC ANALYSIS,

SPECIALLY ADAPTED FOR USE IN THE LABORATORIES OF  
COLLEGES AND SCHOOLS, AND BY BEGINNERS.

BY

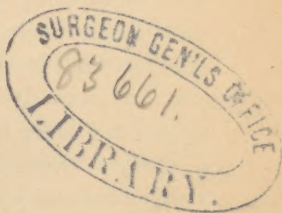
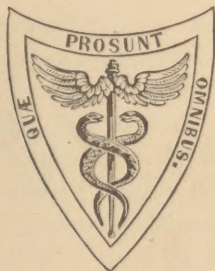
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WITH ILLUSTRATIONS.

FROM THE THIRD ENGLISH EDITION.



PHILADELPHIA:  
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1881.

Annex

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## PREFACE.

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THIS little treatise was commenced to supply a course of Practical Chemistry to my own classes. I was encouraged to proceed with it by finding that a want of a sufficiently elementary and explanatory Laboratory Text-book was very widely felt.

It has been my aim throughout to give all necessary directions so fully and simply as to reduce to a minimum the amount of assistance required from a teacher. The language employed has been rendered simple and intelligible by avoiding the unnecessary use of scientific terms, and by explaining or paraphrasing in ordinary words any such terms when introduced for the first time. The directions how to work, and the descriptions of the preparation and use of apparatus, have been given more fully than is usual, since my own experience, confirmed by that of other teachers, convinces me that one of the most serious hindrances to the utility of many of the smaller Text-books on Practical Chemistry is the too great conciseness of the language employed, which frequently renders it unintelligible to the student unless supplemented by very copious verbal explanation from the teacher.

Whilst making the very desirable amplifications above referred to, the book has been kept within small dimensions, partly by the omission of all such higher instruction as is not required by a student of elementary chem-



istry, and partly by the insertion of the supplementary or merely explanatory portions in smaller type. The text has been supplemented by appendices containing matter suited to more advanced students. I have also thought it best to avoid entering into any lengthy theoretical explanations. The modern teaching of chemistry is in practice very appropriately divided into two departments—namely, theoretical instruction imparted by lectures or by the study of textbooks of theoretical chemistry, and practical instruction imparted in a chemical laboratory by working according to the directions of a practical textbook. Since by this system the student has time and opportunity afforded him for the study of the theoretical and descriptive portions of the science, it is as unnecessary as it is undesirable that his Practical Textbook should tempt him to bestow valuable time in the laboratory upon the study of matters of theoretical—not practical—importance.

The analytical reactions and methods have been carefully worked through from the text by myself and by the members of my classes; the accuracy and intelligibility of their descriptions have thus, I hope, been secured. Only those reactions and methods which are commonly employed for analytical purposes have been entered. I have naturally, in selecting analytical methods for an elementary treatise, felt it desirable that those chosen should be as simple and easy of execution as possible; in some cases, however, methods which are most eligible on these grounds have proved on trial to be so inferior in accuracy and delicacy, that they have been abandoned in favor of others which are recommended by their trustworthiness rather than by their simplicity. In such cases, however, I have also described the more simple methods,

since they may be employed in analyses in which minute quantities of a substance have not to be tested for. The reactions given in an elementary textbook must necessarily be limited as to number, and I have felt it advisable to introduce such reactions as are useful in general analysis rather than those which claim to be merely interesting and instructive.

The book has been divided into seven sections, the contents of which are fully stated on pages ix-xv. The first six contain a good practical course for senior students; this may, however, be modified to suit junior students, or those working with a special object, as is shown in the Introduction.

The seventh section contains full lists of all apparatus, reagents, and chemicals required in working through the different sections; there is also added a list of general apparatus, with a description when necessary of its construction and use. In this section there will also be found full and systematic descriptions of the most simple methods for preparing the different solutions required in analysis, with a statement of the strength most appropriate for each. Experience has proved that these are matters which merit more attention than is usually bestowed upon them. The methods of preparing pure chemicals are omitted, since they may now be readily and cheaply purchased; before using purchased chemicals their purity should, however, always be ascertained by the tests given in this section.

Symbolic notation has been employed, instead of the full chemical names, throughout the sections on analytical chemistry. In its most concise form this chemical shorthand conduces so much to brevity in writing down results that no other plea is required for its use. The

simple plan of labelling each bottle in the laboratory with the chemical formula as well as the name of its contents, will prevent any difficulty arising from this general employment of chemical formulæ.

Special features in the book are the arrangement of all tables *across* instead of *along* the pages; the turning of the book is thus rendered unnecessary—a convenience which will be appreciated by all students of Practical Chemistry.

The “Tables of Differences,” which contain for each Analytical Group a summary of the differences of behavior of its members with reagents, are also special—being an extension of the system employed in Galloway’s “Manual of Qualitative Analysis.”

It is almost superfluous to mention that free use has been made of the standard works of Fresenius and Rose; much valuable information has been introduced from these sources. I have also frequently adopted the very convenient tabular form of entering analytical methods which is employed in Valentin’s “Textbook of Practical Chemistry,” and with the author’s permission have transcribed, with a few trivial alterations, the excellent Phosphate Table devised by him. My acknowledgments are also due to Dr. W. A. Tilden, of Clifton College, and to the Rev. T. N. Hutchinson, of Rugby, and to many other teachers who have suggested valuable improvements.

The book is especially intended to furnish a course of instruction in practical chemistry in the laboratories of our public and other schools. It will thus supply a demand which is rapidly increasing, as the value of a sound elementary instruction in practical science is becoming more widely appreciated, both as a means of mental training and as a preparation for the chemical and medi-



cal professions, as well as for many branches of manufacturing industry and enterprise. The fifth section has been inserted for the use of those who are preparing for practical examinations in which proficiency in the analysis of simple salts only is required of the candidate. This is the standard fixed for the Preliminary Scientific (M.B.) Examination of the London University, and for the more elementary examinations conducted by the Oxford and Cambridge Universities, such as those for school certificates.

The sixth section and appendices, however, contain additional details suited for the analytical work of advanced students, and will be found sufficient to qualify a student for the higher University examinations in qualitative analytical chemistry.

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The present edition has been subjected to a careful revision, and the analysis of simple salts in Section V has been recast in a more simple and systematic form.

F. C.

NEWCASTLE-UNDER-LYME, January, 1880.



# CONTENTS.

## SECTION I.

### EXPERIMENTS ILLUSTRATING THE PREPARATION AND PROPERTIES OF GASES, ETC.

I.	Oxygen, . . . . .	—	19
II.	Hydrogen, . . . . .	—	25
III.	Carbon dioxide, . . . . .	—	29
III a.	Nitric oxide, . . . . .	—	34
IV.	Ammonia, . . . . .	—	34
V.	Carbon monoxide, . . . . .	—	37
V a.	Chlorine, . . . . .	—	39
V b.	Hydrochloric acid gas, . . . . .	—	40
VI a.	Distillation of water, . . . . .	—	40
VI b.	Preparation of nitric acid, . . . . .	—	42

## SECTION II.

### PREPARATION AND USE OF APPARATUS REQUIRED IN ANALYSIS, . . . . .

Bunsen burner, . . . . .	1-19	43
Spirit-lamp, . . . . .	1, 2	43
Blowpipe, . . . . .	3	45
Glass tubes, cutting, . . . . .	4	45
“ bending, . . . . .	5	46
“ drawing out, . . . . .	6	47
Boring corks, . . . . .	7	47
Making sulphuretted hydrogen tube, . . . . .	8	47
Making ignition-tubes, . . . . .	9	48
“ stirring-rods, . . . . .	10	49
Mounting platinum wires, . . . . .	11, 11a	49
Making wash-bottle, . . . . .	12	50
Cleaning glass and porcelain apparatus, . . . . .	13	50
Cleaning platinum foil and wire, . . . . .	14	52
Putting away apparatus, . . . . .	15	53
Heating glass and porcelain: . . . . .	16	53
Porcelain dishes, . . . . .	17	54
Glass vessels, . . . . .	18	54
	19	54



	Paragraph	Page
SECTION III.		
ANALYTICAL OPERATIONS, DESCRIPTIONS ILLUSTRATED BY EXPERIMENTS, . . . . .	20, 35 <i>b</i>	56
Solution, . . . . .	20	56
Evaporation, . . . . .	21	58
Precipitation, . . . . .	22	59
Filtration and decantation, . . . . .	23, 23 <i>a</i>	60
Decantation, . . . . .	23 <i>b</i>	63
Washing precipitates on the filter, . . . . .	24, 24 <i>a</i>	63
"                    "                    by decantation, . . . . .	24 <i>b</i>	64
Drying precipitates, . . . . .	25	64
Removing precipitates from the filter, . . . . .	26	65
Ignition, . . . . .	27	67
Sublimation, . . . . .	28	68
Fusion, . . . . .	29	68
<i>The Use of the Blowpipe:</i> . . . . .	30	69
Borax beads, . . . . .	31	70
Flame colorations, . . . . .	32	71
Ignition on charcoal in the blowpipe flame, . . . . .	33	73
Levigation of residue, . . . . .	33 <i>a</i>	74
<i>The Use of Test-papers:</i> . . . . .	34	75
Making neutral, acid, and alkaline, . . . . .	35, 35 <i>a</i>	77
Turmeric-paper, . . . . .	35 <i>b</i>	78
Fractional solution, crystallization and distillation, . . . . .	—	79
SECTION IV.		
ANALYTICAL REACTIONS, . . . . .	36-329	80
Introductory remarks on analytical classification and on the analytical course which follows, . . . . .	—	80
Analytical classification, . . . . .	36	83
Analytical groups, . . . . .	37	84
Method of trying the reactions, . . . . .	38	84
<i>Entry in the Note-book:</i> . . . . .	39	86
Chemical notation, . . . . .	40	86
Chemical equations, . . . . .	41	87
Rules for drawing out an equation, . . . . .	42	87
Contractions to be employed, . . . . .	43	88
Examples showing method of entry in the note-book, . . . . .	44	89
Rules to be observed whilst working, . . . . .	45	89
Reactions for Metals:		
<i>Group V (Potassium Group):</i> . . . . .	40-67	91
Potassium, . . . . .	47-50	92
Ammonium, . . . . .	51-55	94
Sodium, . . . . .	56, 57	95

	Paragraph	Page
Magnesium, . . . . .	58-63	96
Table of differences and its use, . . . . .	64, 65	97
Principles of separation, . . . . .	66	98
Table for separation and detection, . . . . .	67	100
<i>Group IV (Barium Group):</i> . . . . .	68-89	101
Barium, . . . . .	69-74	101
Strontium, . . . . .	75-79	102
Calcium, . . . . .	80-86	102
Table of differences, . . . . .	87	103
Principles of separation and detection, . . . . .	88	104
Table for separation and detection, . . . . .	89, 433	104
<i>Group III a (Iron Group):</i> . . . . .	90-109	105
Aluminium, . . . . .	91-94	105
Iron, . . . . .	95-101	106
Chromium, . . . . .	102-106	108
Table of differences, . . . . .	107	109
Principles of separation and detection, . . . . .	108	110
Table for separation and detection, . . . . .	109, 436	110
<i>Group III b (Zinc Group):</i> . . . . .	110-141	110
Zinc, . . . . .	111-114	111
Manganese, . . . . .	115-120	112
Nickel, . . . . .	121-128	113
Cobalt, . . . . .	130-137	115
Detection of members separately, . . . . .	138	117
Table of differences, . . . . .	139	117
Principles of separation and detection, . . . . .	140	118
Table for separation and detection, . . . . .	141, 437	118
<i>Group II a (Copper Group):</i> . . . . .	142-176	119
Mercuricum, . . . . .	143-148	119
Lead, . . . . .	149-153	121
Bismuth, . . . . .	154-159	122
Copper, . . . . .	160-168	123
Cadmium, . . . . .	169-172	125
Table of differences, . . . . .	173	125
Detection of members separately, . . . . .	174	125
Principles of separation and detection, . . . . .	175	125
Table for separation and detection, . . . . .	176-435a	126
<i>Group II b (Arsenic Group):</i> . . . . .	177-210	128
Arsenic, . . . . .	179-190	128
Antimony, . . . . .	191-200	136
Tin, . . . . .	201-205	138
Table of differences, . . . . .	206	140
Principles of separation and detection, . . . . .	207	140
Table for separation and detection, . . . . .	208-435b	141
A second method of separation and detection, . . . . .	209	141
A third, . . . . .	210	142
<i>Group I (Silver Group):</i> . . . . .	211-222	143
Lead, . . . . .	[149-153]	[121]
Silver, . . . . .	212-216	144
Mercurousum, . . . . .	217-219	144

	Paragraph	Page
Table of differences, . . . . .	220	145
Principles of separation and detection, . . . . .	221	145
Table for separation and detection, . . . . .	222, 433	145
Reactions for gold, . . . . .	223-224a	146
Reactions for platinum, . . . . .	225, 226	146
<b>Reactions for Acid-radicles:</b> . . . . .	227-329	147
<i>Group I (Sulphate Group),</i> . . . . .	227, 228	148
<i>Group II (Carbonate Group):</i> . . . . .	229-246	149
Carbonates, . . . . .	229	149
Sulphides, . . . . .	230-235	150
Sulphites, . . . . .	236-238	152
Theiosulphates, . . . . .	239-240a	152
Hypochlorites, . . . . .	241, 242	153
Nitrites, . . . . .	243-245	154
Detection of the members when mixed, . . . . .	246	154
<i>Group III (Nitrate Group):</i> . . . . .	247-256	155
Nitrates, . . . . .	247-251	155
Chlorates, . . . . .	252-255	157
Detection when mixed, . . . . .	256	158
<i>Group IV (Chloride Group):</i> . . . . .	257-274	158
Chlorides, . . . . .	257-260	158
Bromides, . . . . .	261-264	161
Iodides, . . . . .	265-270	162
Detection of separate members, . . . . .	271	164
Separation and detection, . . . . .	272-274	165
<i>Group V (Phosphate Group):</i> . . . . .	275-282	167
Phosphates, . . . . .	275-278a	167
Arsenates, . . . . .	279	169
Detection, . . . . .	280-281a	169
Separation and detection, . . . . .	282	170
<i>Ungrouped Acid-radicles:</i> . . . . .	283-302	170
Borates, . . . . .	283-285	170
Chromates, . . . . .	286-289	171
Silicates, . . . . .	290-293	173
Fluorides, . . . . .	294-298	174
Fluosilicates, . . . . .	299-302	176
<i>Organic Acid-radicles:</i> . . . . .	303-329	178
Cyanides, . . . . .	303-306	178
Ferrocyanides, . . . . .	307-310	180
Ferricyanides, . . . . .	311-314	181
Sulphocyanides, . . . . .	315, 316	181
Oxalates, . . . . .	317-319	182
Tartrates, . . . . .	320-325	183
Acetates, . . . . .	326-328	185
<b>SECTION V.</b>		
<b>ANALYSIS OF SIMPLE SUBSTANCES FOR ONE</b>		
<b>METAL AND ONE ACID-RADICLE,</b> . . . . .	330-369	187
Introductory remarks, and tabular classification of metals, . . . . .	330	187



	Paragraph	Page
Preliminary examination of a solid for the metal, . . . . .	331-333	190
Solution of a solid substance, . . . . .	332	191
Preliminary examination of a liquid for the metal, . . . . .	334	196
Preliminary examination for the acid-radicle, . . . . .	335-338a	198
<i>Examination for the metal</i> , . . . . .	339-348	200
General table and notes thereon, . . . . .	339-343	200
Table I (Silver Group), . . . . .	344	202
Table II (Copper and Arsenic Groups), . . . . .	345	203
Table III A (Iron Group), . . . . .	346	204
Table III B (Zinc Group), . . . . .	347	204
Table IV (Barium Group), . . . . .	348	205
<i>Examination for the acid-radicle</i> , . . . . .	349-356	205
<i>Examination of Group III</i> , . . . . .	357-361	209
<i>Examination of a substance with metallic appearance</i> , . . . . .	366	214
<i>Examination of an insoluble substance</i> , . . . . .	367-369	215
<i>Examples of entry of analyses</i> , . . . . .	—	219
SECTION VI.		
FULL ANALYTICAL COURSE AND TABLES, . . . . .	370-487	228
<i>Introductory:</i>		
Separation of metals into groups by group reagents, . . . . .	370	228
Addition of reagents in excess, . . . . .	371	229
Evaporation before precipitating Group III, . . . . .	372	229
General remarks, . . . . .	373, 374	230
Preliminary examinations, their use, . . . . .	375-378	230
<i>General analytical course:</i>		
Preliminary examination of a liquid, . . . . .	380, 381	233
Solution of a non-metallic solid, . . . . .	383-386b	234
Preliminary examination of solids for the metals present, . . . . .	387-409	236
Preliminary examination of solids for acid-radicles, . . . . .	410-418	242
<i>Examination for metals:</i> . . . . .	419-439	246
General table and notes thereon, . . . . .	419-432	246
Table I (Silver Group) and Table G, . . . . .	433, 434	251
Table II (Copper and Arsenic Groups), . . . . .	435	252
Table III A (Iron Group), . . . . .	436	254
Table III B (Zinc Group), . . . . .	437	255
Table IV (Barium Group), . . . . .	438	256
Table V (Potassium Group), . . . . .	439	259
<i>Examination for acid-radicles</i> , . . . . .	440-454	261
<i>Table showing solubility of substances in water and acids</i> , . . . . .	455-458	266
<i>Remarks on the precipitation of Group III</i> , . . . . .	459-462	269
Rules for the precipitation and examination of Group III, . . . . .	463	272

	Paragraph	Page
Table III c <sub>1</sub> (Iron and Zinc Groups mixed), . . . . .	464	273
Table III c <sub>2</sub> (Iron and Zinc Groups mixed), . . . . .	465	274
Table III D (Phosphates in Group III), . . . . .	466	276
<i>Examination of substances with metallic appearance,</i> . . . . .	467-471	278
<i>Separation and detection of gold and platinum,</i> . . . . .	472-474	281
<i>Examination of substances insoluble in water and acids,</i> . . . . .	475-479	283
<i>Analysis of silicates,</i> . . . . .	480, 481	287
<i>Analysis of substances containing cyanogen,</i> . . . . .	482-487	289
<i>Example showing how to enter analytical results,</i> . . . . .	488-493	290

## SECTION VII.

APPARATUS AND CHEMICALS REQUIRED FOR  
THE PRECEDING COURSE, . . . . .

THE PRECEDING COURSE, . . . . .	494-539	301
<i>List of apparatus for each student,</i> . . . . .	494	301
<i>List and description of general apparatus:</i> . . . . .	495-506	304
Indigo-prism, cobalt-glass, cork-borers, . . . . .	496-498	304
Sulphuretted hydrogen apparatus, . . . . .	499, 500	304
Passing sulphuretted hydrogen, . . . . .	500a	307
Agate mortar, leaden or platinum crucible, . . . . .	501, 502	308
Steam-oven, water-bath, tubulated flasks, . . . . .	503-505	308
Distillation of water, . . . . .	506	311
Recovery of the metals from silver and platinum residues, . . . . .	507, 508	314
<i>Directions for preparation of reagents and solutions:</i> . . . . .	509-517	316
Introductory remarks, . . . . .	509, 510	316
Dilution of liquids, . . . . .	511	316
Solution of solids, . . . . .	512-515	317
Preparation of solutions for the reactions, . . . . .	516, 517	320
<i>Lists of the reagents, solutions, and chemicals, stating their condition or strength and special processes of preparation:</i> . . . . .	518-533	321
Introductory and explanatory remarks, . . . . .	518-521	321
Labelling and varnishing, . . . . .	522, 523	322
List of reagents for each bench, . . . . .	524	324
List of reagents, for general use, . . . . .	525, 526	324
Preparation of saturated solutions of solids, . . . . .	527	330
“ “ “ of gases, . . . . .	528	331
Lists of solutions required for Section IV, . . . . .	529, 530	334
List of chemicals required for Section I, . . . . .	531	338
List of chemicals required for Section III, . . . . .	532	339
List of sundry other requisites, . . . . .	533	340
<i>Examples of substances to be given for analysis,</i> . . . . .	534-539	341

	Paragraph	Page
APPENDIX I.—Reactions and detection of the rarer elements, . . . . .	540-554	345
Group I ( <i>Silver Group</i> ): . . . . .	540, 541	345
Thallium, . . . . .	540	345
Tungstates, . . . . .	541	346
Group II a ( <i>Copper Group</i> ): . . . . .	542	346
Palladium, . . . . .	542	347
Group II b ( <i>Arsenic Group</i> ): . . . . .	543-545	347
Molybdates, . . . . .	543	347
Selenium, . . . . .	544	348
Tellurium, . . . . .	545	348
Group III ( <i>Iron and Zinc Groups</i> ): . . . . .	546-550	349
Uranium, . . . . .	546	349
Indium, . . . . .	547	349
Beryllium, . . . . .	548	350
Titanium, . . . . .	549	350
Vanadium, . . . . .	550	351
Group V ( <i>Potassium Group</i> ): . . . . .	551, 552	352
Lithium, . . . . .	551	352
Rubidium and Cæsium, . . . . .	552	352
General table for detection of the rarer elements, . . . . .	553	354
Table for examination of Group III for the rarer elements, . . . . .	554	356
APPENDIX II.—The spectroscope, its use in analysis, . . . . .	555, 556	358
Spectrum-chart, . . . . .	557	360
APPENDIX III.—List of chemical elements with symbols and atomic weights, . . . . .	558	362
Thermometric scales, . . . . .	559	362
Weights and measures—French and Eng- lish, . . . . .	560, 561	363



# PRACTICAL AND ANALYTICAL CHEMISTRY.

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## INTRODUCTION.

THE course of practical chemistry which should be pursued by a student depends partly upon his object in studying the science, and partly upon the time and means which he has to devote to the study. The first four sections and the sixth furnish a good general course for a senior student who wishes to obtain a training in practical and analytical chemistry; but for younger students, after completing the first three sections, the most suitable analytical course consists in trying through the reactions in Section IV, and as the reactions for each group are completed, testing several substances containing only one member of the group for the metal present by the table of differences. The analysis of simple substances by Section V may then be worked through, and, after becoming familiar with this, separations of the mixed members in each group are done, leading thus to Section VI. The modification which should be made in the student's course to suit individual cases will, perhaps, be most readily understood by stating the objects of each section in the book:

SECTION I is adapted to impart experience in chemical manipulation, and to afford practical illustrations of the elementary portions of theoretical or descriptive chemistry; it may be omitted when instruction in analysis only is required.

SECTION II is indispensable, and must be carefully perused.



SECTION III is also indispensable to the student of analytical chemistry, but if the time at his disposal is *very limited*, he may omit the performance of the experiments described in this section, and merely read through the text.

SECTION IV must be carefully worked through. A student whose time is limited may, however, simply try the reactions and omit the performance of analyses at the end of each group.

SECTION V is intended for students whose object is to learn only the analysis of simple salts, such as is required in many modern examinations on practical chemistry.

This section may also be used as an easy beginning in analysis, and as an introduction to more complicated analyses to be made by Section VI, or it may be passed over by the student who is intending to learn general analysis.

SECTION VI is not required by a student who is learning only the analysis of simple salts, but should be carefully worked through by the student of general analysis, who may, after becoming thoroughly conversant with its contents, pass on to quantitative analysis, or to any special branch of practical chemistry he may require.

## SECTION I.

### EXPERIMENTS ILLUSTRATING THE PREPARATION AND PROPERTIES OF GASES, ETC.

*Introductory Remarks.*—In this section full directions are given for the preparation of five gases (viz., oxygen, hydrogen, carbon dioxide, ammonia, and carbon monoxide) and for certain interesting and instructive experiments which may be made with them. The processes of preparation and manipulation required for these gases are more or less typical of those employed for all other gases, and the student will, therefore, from the experience obtained by performing the experiments with the above-named gases, easily prepare and experiment upon the three other gases (nitric oxide, chlorine, and hydrochloric acid, by following the directions inserted in small print, and any other gas by the account given of it in a treatise on chemistry. Those gases which are in small type may be omitted in the practical course. Two examples of the process of distillation are also appended.

The reference numbers inclosed in brackets refer to the paragraphs which commence with Section II (p. 43); the numbers will be found in thick type in the text, and at the head of each page the numbers of the paragraphs are also placed in square brackets.

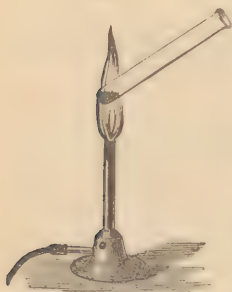
A full list of the apparatus required for this section is given in par. 494, and its use is explained in pars. 1-10 and 14-19; a list of chemicals and certain other requisites will be found in par. 531.

*Note.*—The student must carefully read through the whole description of each experiment before beginning to perform it, and after its successful performance should enter a brief description of it in his note-book.

**I. OXYGEN GAS.**—When iron is for some time exposed to moist air its surface becomes covered with rust; many other metals undergo a similar change in moist air, but the alteration produced in their appearance is not usually so noticeable as in the case of iron. The liquid metal mercury does not rust as iron does in moist air, but it becomes slowly covered with red mercury rust when strongly heated for some time in a flask open to the air; this mercury rust has received the name of mercuric oxide. The fact that metals become heavier by rusting proves that something is added during the process.

EXP. 1.—Place in a clean and perfectly dry test-tube sufficient mercuric oxide to cover the bottom; heat the powder (1, 19) as shown in Fig. 1, loosely stopping the end of the tube with the thumb. As soon as small drops

FIG. 1.

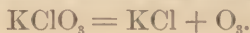


of mercury form on the sides of the tube, remove the thumb and quickly place inside the top of the tube the burning end of a slip of wood (*e. g.*, the uncoated end of a wooden lucifer match); the flame will be seen to burn more brightly. If, after again heating the powder for some time in the way just described, the slip be introduced into the mouth of the tube immediately after blowing out the flame and whilst there is a spark at its end, the glowing end will be caused to burst into flame. This behavior with a burning or glowing slip of wood is one of the most remarkable properties of oxygen gas, and we frequently make use of this property as a “test” for its presence. The chemical change which has occurred is thus represented by an equation :



Since by heat, then, we can separate from mercuric oxide mercury and oxygen, we learn that the process of rusting consists in the metal taking oxygen gas from the air, and the increase of weight above referred to is thus accounted for; if all metal rusts could be decomposed by heat we might obtain oxygen from them just as from mercuric oxide. This method of making oxygen is interesting, since it was the first means known of preparing the gas; it is never used nowadays to prepare large quantities of oxygen, since other substances are known which contain a larger proportion of oxygen, and give it off, when they are heated, more easily than mercuric oxide does—substances which are also preferable on account of their greater cheapness.

Potassium chlorate is most frequently employed :



EXP. 2.—Place in a clean dry test-tube a little potassium chlorate, and heat it as in Exp. 1. The white salt, after “decrepitating” or crackling, “fuses” or melts, and when further heated appears to boil; the small bubbles which are given off consist of oxygen gas, as may readily be proved by holding in the mouth of the test-tube a burning or glowing splinter of wood as described in Exp. 1.

Potassium chlorate gives off oxygen gas much more readily than does mercuric oxide; but if it is mixed with small quantities of certain other substances, which themselves appear to undergo no change, its oxygen is driven off by heat with extreme facility; of these substances, manganic oxide or black oxide of manganese is the one usually chosen.

EXP. 3.—Powder some potassium chlorate (about as much as would fill a watch glass) finely in a mortar, mix with it, by rubbing them together in a mortar, about one-fifth as much powdered manganic oxide, and heat a small quantity of the mixture in a test-tube; the oxygen will begin to come off as soon as the mixture is heated, and a comparatively gentle heat will cause the gas to be rapidly evolved.

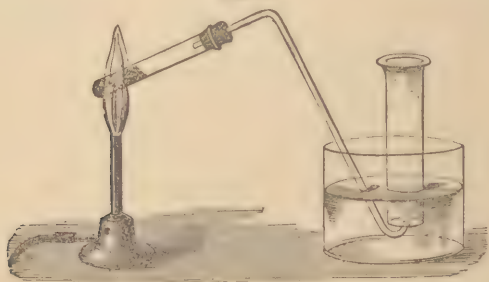
In the preceding experiments the oxygen was detected in the tube in which it was prepared, and was allowed to pass away freely into the air. When the gas has to be collected in a vessel unmixed with air, it is made to pass through a bent glass tube (the delivery-tube), which is fitted by means of a cork air-tight into the mouth of the test-tube; the end of this tube dips into some water, and the bubbles of gas are allowed to rise into a vessel full of water and inverted over the end of the delivery-tube. This process of “collecting” oxygen is fully described in the following experiment; in the performance of which two students may advantageously work together, one attending to the regulation of heat to the mixture, the other to filling the gas-jars.

EXP. 4.—Select a sound cork, of such a size that, after having been softened by being squeezed or by being rolled with gentle pressure on the floor under the foot, it fits



tightly into the mouth of the test-tube to be employed. Then bend (6) a piece of hard glass tubing, about 14 inches in length, into the form shown in the figure ; so adapting the bends by trial that when the apparatus is fitted together the bottom of the test-tube may be at a convenient height in the flame, the end of the delivery-tube at the same time dipping about an inch under water. Make a hole through the centre of the cork (8), of such a size that the glass tube fits tightly into it. Then test whether the apparatus is air-tight by fitting the glass tube into the cork, and the cork into the test-tube, and blowing down the open end of the delivery-tube ; no air must be heard to escape, or must be seen to bubble out on moistening

FIG. 2.



the cork ; if air does escape, a fresh cork must be taken. Now pour into the perfectly dry test-tube the oxygen mixture (see Exp. 3) off a piece of paper folded into a trough, or scoop up the mixture from the mortar with the mouth of the test-tube, until the tube is about one-third full, and fit in the cork and delivery-tube.

Before heating the tube fill the jar in which the oxygen is to be collected with water, close it with a stopper or ground-glass plate or with the hand, invert its mouth in water three or four inches in depth, contained in an earthenware pan or bowl, and carefully remove the stopper or plate. If this operation has been performed with proper precaution the jar will be entirely filled with water, and no air-bubble will remain. Next proceed to heat

the upper part of the oxygen mixture, holding the tube in one hand and keeping the lamp slowly moving with the other hand, in order to prevent any part of the glass from being suddenly and strongly heated, which would be liable to crack it. Oxygen gas will soon be evolved, but will not at once appear at the end of the delivery-tube, since it has first to drive out the air which filled the apparatus; as soon as a slip of wood glowing at its end is kindled when held at the mouth of the delivery-tube, the oxygen has driven out the air and is beginning to escape; the end of the delivery-tube is then at once dipped under water beneath the mouth of the jar, and the stream of bubbles rising into it will rapidly displace the water. As soon as the jar is full of gas, close its mouth under water with the stopper or glass plate, and remove it for experiment. The jar may also be removed by slipping under its mouth a small dish or saucer; the water taken out in the saucer then closes the mouth of the jar air-tight.

*Precautions.*—The water must be removed from the pan, when it rises inconveniently high, by means of a small porcelain dish; if at any time the gas should be given off too rapidly, the flame should be removed until the current slackens; the lower portions of the mixture should be heated only after the upper parts refuse to yield any more gas: when the process is to be stopped, the end of the delivery-tube must be removed from the water before the gas has ceased to bubble out, and the test-tube must not be allowed to touch cold or wet objects, which would cause the hot glass to crack.

Several bottles filled with oxygen will be required for the following experiments, or the same bottle may, if necessary, be refilled with the gas according to the above directions, after the completion of each experiment.

*Note.*—The use of ground-glass plates, which must close the mouth of the jar perfectly air-tight, is much easier than that of stoppers. An earthenware "beehive shelf," which may be used in a common earthen pan, or a "pneumatic trough," is also convenient, since it supports the jar during the process of collection.

Oxygen gas is remarkable for the energy with which

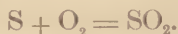
it combines with or burns many substances; three examples are given of this property in Exps. 5, 6, and 7.

EXP. 5.—Select a splinter of wood charcoal or a small piece about the size of a nut; the experiment is more brilliant if the surface of the charcoal formed originally part of the bark of the tree. Bind this upon a “deflagrating spoon” with a little fine iron or copper wire; then adjust the wire handle of the spoon in the brass cap, so that when held beside the bottle of oxygen with the cap on a level with the mouth of the jar, the little metal cup is about an inch from the bottom of the bottle. Now heat the charcoal in the Bunsen flame, or better in the blowpipe flame (4), until a part of its surface glows when held in the air, and quickly place it in the bottle of oxygen, with the brass plate covering the mouth of the bottle. (See Fig. 7, p. 33.) The charcoal will burn much more brilliantly than in air, throwing off sparks if its surface was “barky:”



When it ceases to burn, pour into the bottle a little clear lime-water from a small beaker or test-tube, quickly close the bottle, and shake the liquid round inside it; the clear liquid becomes milky, indicating the presence of carbon dioxide gas, as will be hereafter explained.

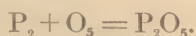
EXP. 6.—Remove the charcoal from the deflagrating spoon and replace it by a piece of sulphur as large as a pea; heat the spoon in the flame until the sulphur melts and begins to burn with a pale-blue almost invisible flame. Then place the spoon in a fresh jar of oxygen; the sulphur will at once burn with a much brighter flame, which emits a beautiful violet light:



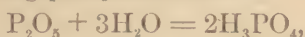
Sulphur dioxide or sulphurous anhydride gas remains in the bottle; its presence is proved by its suffocating smell, also by pouring a little water into the bottle and shaking it round. Sulphurous acid is thus formed, and is recognized by dropping into the water a piece of blue litmus-paper, which is immediately reddened, and by pouring

in a few drops of red potassium dichromate solution, the color of which changes to green.

EXP. 7.—Cleanse the deflagrating spoon from any remaining sulphur, and put into it a small piece of phosphorus no larger than a pea. The phosphorus may be cut with a knife; it must be touched only with *wet* fingers, and should be handled as little as possible, since it is liable to catch fire by the heat of the hand; it is always kept under water, being dried only immediately before being used by pressing it between filter-paper or blotting-paper, or with a dry cloth. Set fire to the phosphorus by holding the spoon in the flame, and notice how it burns in the air; then place the spoon in a jar of oxygen—the phosphorus will burn most brilliantly, producing a white substance called phosphorus pentoxide, or phosphoric anhydride:



When the phosphorus has ceased to burn, pour in a little water and shake it round in the jar, the white substance dissolves, yielding phosphoric acid:



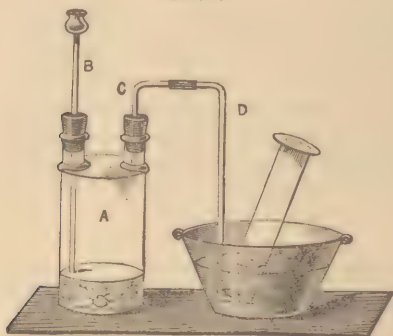
and the water may now be proved to be acid by dropping into it a piece of blue litmus-paper, which will be immediately reddened.

*Tests for Oxygen.*—A convenient test for oxygen is to introduce into the gas a slip of wood with a spark at the end, which is caused to burst into flame. Only one other gas possesses this property, and it is readily distinguished from oxygen by other means. This test only detects oxygen when it is in a pretty pure condition.

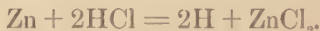
II. HYDROGEN GAS.—The liquid substance water consists of oxygen gas combined with another gas called hydrogen; several processes are known for preparing hydrogen from water. This gas is, however, most readily obtained from another liquid containing it, called hydrochloric acid, by the action upon it of the metal zinc.

EXP. 8.—Fit a two-necked Woulffé's bottle<sup>1</sup> (A, Fig. 3) with air-tight, perforated corks, bearing a thistle funnel (B), whose end reaches nearly to the bottom of the bottle, and a tube bent, as shown at C, and terminating just below the cork; join to this, by means of a short piece of tightly fitting india-rubber tube, a bent delivery-tube, D. Pour into the bottle sufficient granulated

FIG. 3.



zinc to cover the bottom, replace the corks, and, after ascertaining that the apparatus is air-tight by closing the end of the delivery-tube and blowing down the thistle funnel, pour in through the funnel sufficient water to cover the zinc and the end of the funnel-tube; then add strong hydrochloric acid gradually until, after mixing the acid and water by shaking the bottle, the hydrogen is seen to rise from the zinc in numerous small bubbles:



Then dip the end of the delivery-tube under water contained in the pan or trough, and allow the gas to bubble out through the water for at least five minutes. This delay is necessary in order to give the hydrogen time to entirely remove the air which filled the bottle, and which,

<sup>1</sup> A wide-necked bottle may be used instead, being fitted as shown in Fig. 5 (p. 30).



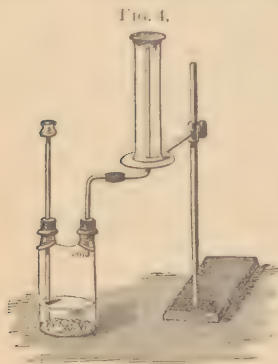
when mixed with hydrogen, produces a dangerously explosive mixture. Before collecting larger quantities of the gas for experiments ascertain that the hydrogen is no longer mixed with air by inverting a test-tube filled with water over the end of the delivery-tube. As soon as the tube is full of gas close its mouth with the thumb and hold it to a flame; if the gas burns with a slight explosion, the tube is again similarly filled with the gas and tried in the same way. As soon as the gas burns quietly with a pale flame, a small thick glass cylinder or tube may be filled with it in the same way as was directed for oxygen.

If during the preparation of gas for the following experiments the gas comes off too slowly, it is only necessary to pour in a little more strong acid through the funnel and mix it with the liquid in the bottle by gently shaking the latter.

EXP. 9.—Hold the vessel filled with hydrogen with its mouth open and directed upwards for a short time, the gas will entirely escape; the absence of the gas may be shown by holding a lighted taper in the vessel, when no flame will be seen at the mouth. If the cylinder be refilled with hydrogen and held for a short time mouth downwards, the hydrogen will remain in it, and its presence may be shown by the gas burning with a pale flame when a lighted taper is introduced. These results prove that hydrogen is much lighter than air, since its tendency to rise prevents it from passing out downwards through the open mouth, whilst it readily escapes upwards from the erect cylinder. Since hydrogen is so much lighter than air, it is possible to collect the gas without using water by a process called “displacement.” The delivery-tube of the hydrogen apparatus is passed up to the top of the inverted jar containing air, the hydrogen rises to the upper part of the jar and gradually pushes out the heavier air downwards.

EXP. 10.—Fill a jar with hydrogen by “displacement.” For this purpose fit upon the india-rubber joint of the hydrogen apparatus a delivery-tube bent as shown in Fig. 4, and when a brisk effervescence of gas has been

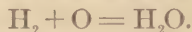
caused by pouring in some strong hydrochloric acid, pass this tube up to the top of an inverted jar and allow the



jar to remain in this position for several minutes; it is best to loosely close the mouth of the jar during this process by letting it rest upon a perforated disk of cardboard, or upon the round brass cap of a deflagrating spoon, supported upon a retort stand ring, or upon an iron tripod stand, since the entrance of air by "diffusion" is thus almost entirely prevented.

Remove this jar, keeping it mouth downwards, and push up inside it a burning wax taper five or six inches in length. The hydrogen will be lighted and will burn with a pale flame at the mouth of the jar, but the flame of the taper will be seen to be extinguished by the gas. The taper may, however, be rekindled by holding it in the hydrogen flame burning at the mouth of the jar.

EXP. 11.—Cover the bottle and funnel-tube with a cloth, to prevent accident in case of an explosion, and light the hydrogen at the end of the delivery-tube used in the last experiment. Hold over the flame a perfectly clean, dry, and cool tumbler or beaker; the inside will become dimmed with moisture, showing that hydrogen gas burning in the air produces water:



*Note.*—Since all gases which have been in contact with water contain more or less vapor of water, or are "moist," it is usual to employ for this experiment a stream of hydrogen gas which has been freed from moisture or "dried." A gas is dried or "desiccated" by passing it through some substance which readily absorbs moisture. Strong sulphuric acid (oil of vitriol), calcium chloride, and quicklime are the desiccating agents most commonly employed. The gas may be made to bubble through strong sulphuric acid contained in a bottle, B (Fig. 10, p. 38), connected, as shown in the figure, with the generating apparatus. It may be also dried by passing it through a tube containing fragments of calcium chloride, or of quicklime

(Fig. 10 *a*), or pieces of pumice-stone moistened with strong sulphuric acid. The moistened pumice may be contained in a U-tube (Fig. 10*b*), or in the bottle B (Fig. 10, p. 33).

EXP. 12.—Measure the height of a short, thick glass cylinder, and divide it into three equal parts by small pieces of gum-paper stuck upon the outside. Fill the cylinder with water, and, after inverting it in water, fill one-third with oxygen (Exp. 4), and the remainder with hydrogen (Exp. 8); let the jar stand with its mouth under water for five or six minutes to allow the gases to mix; then apply a lighted taper to the mouth of the jar directed downwards, taking care not to place the fingers beneath it: the gases combine to form water with a loud explosion.

*Test for Hydrogen.*—Hydrogen gas is recognized by burning with a pale flame in air or oxygen, the flame depositing water on any cold object held above it.

III. CARBON DIOXIDE GAS, OR CARBONIC ANHYDRIDE.<sup>1</sup>—When carbon was burnt in oxygen (Exp. 5) a gas called carbon dioxide remained in the jar; the gas may be prepared in this way, but a much more easy method consists in pouring hydrochloric acid upon some pieces of marble.



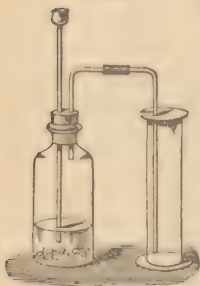
Chalk or limestone may be substituted for marble, but these do not answer so well.

EXP. 13.—Rinse out the apparatus used for preparing hydrogen, and place in it some small pieces of marble; fit into the india-rubber joint a delivery-tube bent at right angles, as shown in Fig. 5; then pour through the funnel-tube sufficient water to cover the marble and the end of the funnel-tube, and then strong hydrochloric acid until gas comes off with brisk effervescence. Place the delivery-tube in a jar, with its end nearly touching the bottom; cover the mouth of the jar with a small disk of

<sup>1</sup> Formerly called carbonic acid, a name which is incorrect, since all acids contain hydrogen.

cardboard which has had a slit cut in it for the delivery-tube, or pass the delivery-tube through the brass cap of a deflagrating spoon, and allow the apparatus to stand for several minutes.

FIG. 5.



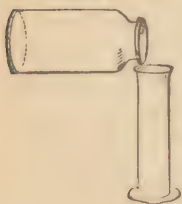
Carbon dioxide being much heavier than air will soon fill the jar by "displacement;" that is to say, it will collect in the lower part of the jar, and, by gradually rising in it, will lift out the air. Since this gas has the property of extinguishing a burning taper, it is easy to ascertain when the jar is full by holding a lighted taper just inside its mouth; if the flame is extinguished, the carbon dioxide has reached the

top. Carbon dioxide gas, being very largely dissolved by water, is rarely collected over water, the process of "displacement" being preferable.

EXP. 14.—Allow this jar of carbon dioxide to stand uncovered and with its mouth upwards for a few minutes; then place in the jar a burning taper; the carbon dioxide is shown to be still present in the vessel by the immediate extinction of the flame. Then hold the jar for several minutes, with its mouth downwards; on testing with a lighted taper only air will be found in the vessel. These experiments prove that carbon dioxide is heavier than air, since it remains in a vessel which is open above, and falls out of one which is open below.

EXP. 15.—Since this gas is so much heavier than air, it can be poured from vessel to vessel like

FIG. 6.

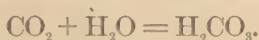


water. This may be shown by pouring carbon dioxide from a bottle filled with the gas into a jar full of air, the latter being somewhat the smaller. The bottle is gradually tilted a little beyond the horizontal position, with its mouth over that of the jar. After holding it in this position for a short time it may be proved by a lighted taper that the gas has left the bottle and is present in the jar.

EXP. 16.—Pour a little lime-water from a test-tube or small beaker into a jar of carbon dioxide and shake the liquid round in the jar. The lime-water will at once become milky, owing to the lime which is dissolved in the water being converted by the carbon dioxide into chalk (calcium carbonate), which, being an insoluble substance, remains mixed as a white powder or “precipitate” with the water:



EXP. 17.—Carbon dioxide gas readily dissolves in cold water, forming a liquid which probably contains carbonic acid:



The solubility of the gas in water may be proved by displacing the air from a bottle, previously half filled with cold water, by carbon dioxide; then tightly closing the mouth of the bottle with the wetted palm of the hand, and shaking vigorously for a short time; the bottle will adhere to the hand, owing to a partial vacuum being produced by the absorption of the gas by the water. A further proof is afforded by dipping the end of the delivery-tube (Fig. 5) to the bottom of a beaker containing water, so as to cause the gas to bubble through the liquid. After the bubbles have passed for several minutes the water may be shown to contain carbonic acid by pouring some of it into a test-tube and adding a little lime-water, which will cause a milkiness;<sup>1</sup> also, by adding to another part of the carbonic acid solution several drops of blue litmus solution, or dipping into it a piece of blue litmus-paper, which will become red, indicating the presence of an acid; keep this liquid. If this liquid containing carbonic acid be tasted it will be found to possess a taste resembling that of soda-water, and in fact soda-water is merely water which contains a large quantity of carbonic acid, as may be proved by examining it with lime-water and litmus. If some of the water containing carbonic acid be boiled in a test-tube, the carbon dioxide gas is driven off again; the bubbles of gas are seen rising in

<sup>1</sup> Sometimes the milkiness disappears, for reasons explained in Exp. 18, unless much lime-water is added.



the water long before the latter boils, and after the liquid has been boiled briskly for several minutes it may be proved to be free from carbonic acid by giving no milkiness on addition of lime-water, and by not changing the color of blue litmus-paper or solution. The red liquid prepared by adding blue litmus to the carbonic acid solution will also become blue when it is boiled.

EXP. 18.—Dilute some lime-water, contained in a small beaker, with an equal quantity of distilled water, and allow the carbon dioxide gas to bubble through it as in Exp. 17; a milkiness will be produced owing to the formation of chalk (Exp. 16); but if the gas is allowed to bubble for several minutes through the liquid, the milkiness will gradually disappear, since the chalk dissolves entirely in the carbonic acid which is formed by the carbon dioxide dissolving in the water. On boiling some of this clear liquid it again becomes milky, since the carbon dioxide is driven out of the water by heat, and therefore the chalk can no longer remain dissolved. It will be found, on pouring out the water, that part of the chalk remains adhering to the inside of the tube, whence it may be removed by pouring in a few drops of hydrochloric acid. The above experiment explains the origin of the coating or “incrustation” of chalk inside kettles and steam-boilers in which chalk-water is boiled. Such water contains chalk dissolved by carbon dioxide gas present in the water; this gas is driven off when the water is boiled, and a great part of the chalk separates upon the sides of the vessels.

*Tests for Carbon Dioxide.*—It is evident that the presence of carbon dioxide gas is shown by its properties of extinguishing a burning taper, and turning lime-water milky; these are the ordinary “tests” for carbon dioxide. We may now proceed to employ them to prove that carbon dioxide is evolved from our lungs during the process of respiration, and also that it is produced by a burning candle.

EXP. 19.—Invert a bottle full of water in a pan of water, and fill it with air from the lungs by blowing the breath out through a glass tube, one end of which is dipped into the water and held beneath the mouth of the

bottle. In order to obtain air *from the lungs* a full breath should be drawn, and the nose then closed by pinching it with the finger and thumb. Before allowing any breath to pass up into the bottle, the greater portion should be breathed out through the tube so as to replace the air contained in the windpipe, mouth, and tube by air from the lungs; the remainder of the breath is then allowed to bubble up into the bottle. Close the bottle, remove it from the pan, and introduce into it a lighted taper; the flame will be immediately extinguished.

Now blow air *from the lungs*, obtained as just described, through a glass tube into lime-water contained in a small beaker; the lime-water will become milky.

EXP. 20.—Fasten a small piece of candle or wax taper upon the deflagrating spoon, and place it alight in a bottle of air, the mouth of which is closed by the brass plate (Fig. 7). After burning for a short time the flame will be extinguished, and if re-lighted will be again extinguished when placed in the jar. Now pour in some lime-water from a small beaker, and shake it round in the bottle; the liquid will be rendered milky.

A similar experiment may be performed, substituting for the candle the flame of coal-gas which is burnt from a jet inside the inverted bottle, and closing the mouth of the bottle with a glass plate, as soon as the flame is extinguished. The extinction of the flame, and the milkiess then produced by shaking the lime-water in the bottle, will prove the production of carbon dioxide by the combustion.

Hence carbon dioxide gas is constantly being introduced into the air by respiration and combustion, and we should therefore expect to be able to detect its presence in air by the above tests. It is manifestly not present in sufficient quantity to extinguish a burning taper, but the presence of carbon dioxide in air may be shown by lime-water in the following way :

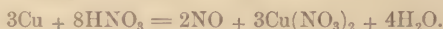
FIG. 7.



EXP. 21.—Pour some clear lime-water into a watch glass, or better a clock glass, and allow it to stand for a few minutes in the air; a film of chalk will gradually form on the surface, and will be seen as white flakes when the water is stirred.

III. *a.* Nitric oxide gas may be prepared in the apparatus used for making carbon dioxide (Fig. 5, p. 30).

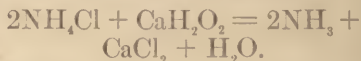
EXP. 22.—The pieces of marble are removed and the apparatus washed out. Some scraps of copper (copper clippings or turnings) are then placed in the flask, and nitric acid diluted with an equal measure of water poured in:



A reddish-brown gas soon fills the inside of the vessel, and should be allowed to bubble off for a time through water; it may then be collected over water as was directed for hydrogen gas. Nitric oxide is colorless, but it forms a reddish-brown gas (chiefly nitrogen tetroxide) when mixed with free oxygen. This is shown by filling a jar with the gas over water, and then allowing it to stand with its mouth open in the air; the entrance of the oxygen of the air at once produces red fumes. The appearance of red fumes in the preparation vessel is thus explained, since the vessel is at first filled with air, with which the first portions of the gas mingle.

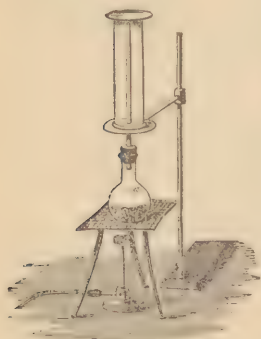
IV. AMMONIA GAS.—The familiar smell of common “smelling salts” is due to ammonia gas, which is constantly being given off from the solid “carbonate of ammonia” contained in the bottle. The gas

is thus evolved only very slowly; it may be made to come off much more rapidly if the “carbonate of ammonia” is mixed with lime and the mixture is then gently heated. Sal ammoniac is usually employed instead of the carbonate of ammonia:



EXP. 23.—Powder some ammonium chloride or sal ammoniac in a mortar, and mix with it thoroughly on a sheet

FIG. 8.



of paper about an equal quantity of slaked lime in fine powder. Pour some of this mixture into a small flask (Fig. 8) until it is about one-third filled, and close the neck of the flask with a tightly fitting perforated cork, into which is inserted a straight piece of glass tube eight or nine inches long. Heat the mixture gently by placing the flask upon a piece of wire gauze on a tripod stand and putting underneath it a lighted rose-burner. Ammonia gas will soon be smelt issuing from the end of the tube, and, since it is much lighter than air, may be collected by "displacement," as seen in Fig. 8. To ascertain when the vessel is filled with the gas it is only necessary to hold at the mouth of the jar a piece of moistened red litmus or yellow turmeric paper; since ammonia gas changes the color of the former to blue and of the latter to reddish-brown, it is easy to see whether it has reached the mouth of the jar by observing whether any change is produced in the color of the paper.

A more easy way to prepare ammonia gas for the following experiments consists in heating a little "Liquor Ammoniae Fortissima" in the flask (Fig. 8) instead of the solid substances.

Ammonia gas does not burn continuously in air at the ordinary temperature, but it burns readily either in strongly heated air or when lighted in oxygen gas. Show this by holding the end of the delivery-tube, from which a stream of gas is issuing, in the top of a Bunsen flame; a pale yellowish-green flame of burning ammonia will be seen; and if the end of the tube is dipped into a jar of oxygen, the ammonia may be inflamed as it issues into the oxygen gas.

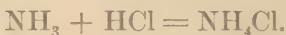
Ammonia should always be collected by displacement, since it is extremely soluble in water, and therefore its collection over that liquid would lead to great waste of the gas. For this reason, also, the vessels in which ammonia is to be collected should always be perfectly dry inside.

EXP. 24.—Place a jar full of ammonia mouth downwards in a vessel of water, and gently shake the jar so as to agitate the water at its mouth; the water rapidly absorbs

the gas and rises in the jar to fill the space formerly occupied by the gas.

If a little water be rapidly poured into a jar of ammonia by momentarily partly opening it and at once covering it again with a glass plate or with the hand, and the water be then shaken in the jar, the water, owing to its having absorbed the gas, will, when poured out, be found to have acquired the smell and behavior with litmus and turmeric papers which characterize the gas. This liquid is in fact weak "Liquor Ammoniae," a solution prepared in large quantities by letting ammonia gas bubble for some time through cold water. When this solution is boiled the ammonia gas is in great part expelled.

Exp. 25.—Pour into a glass jar a little strong hydrochloric acid, close the jar with a glass plate, and shake the acid about inside the jar,—hydrochloric acid gas will thus be liberated; the liquid may then be allowed to run out by slipping aside the glass plate for a moment. Place this jar in an inverted position over a jar containing ammonia gas, and covered with a glass plate (Fig. 9 *a*), then withdraw the glass plates, so that the mouths of the jars are in contact (Fig. 9 *b*), and the hydrochloric acid and ammonia gases can freely intermingle. Dense white fumes of solid ammonium chloride will immediately be formed:



This experiment may also be performed by dipping a glass rod into some strong hydrochloric acid, and holding it in ammonia gas as it issues from the delivery-tube of the apparatus, or in a jar previously filled with the gas; the same white fumes will at once appear.

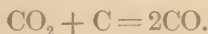
*Tests for Ammonia Gas.*—Ammonia gas may be readily recognized by its pungent smell, by turning moistened red litmus-paper blue and moistened turmeric-paper



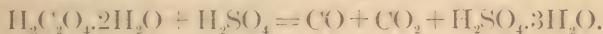
reddish-brown, and also by giving white fumes with a glass rod moistened with *strong* hydrochloric acid.

*Gases are frequently made to pass through certain liquids, in order to free them from impurities before they are collected; this is termed "washing" a gas. In some cases gases are purified by causing them to pass over pieces of a solid substance, which absorbs the impurities. The preparation of carbon monoxide gas from oxalic acid will serve to show how these processes are performed.*

V. CARBON MONOXIDE.—This gas is produced when carbon dioxide gas is made to pass over red-hot charcoal:



It is often thus formed in open grates, and is seen burning at the top with its characteristic blue flame. Carbon monoxide is usually prepared by heating solid oxalic acid with strong sulphuric acid, when a mixture of carbon monoxide and carbon dioxide is given off:



EXP. 26.—Place a little solid oxalic acid in a test-tube; pour upon it strong sulphuric acid<sup>1</sup> sufficient to cover it to a depth of at least half an inch, and heat the mixture. After a short time effervescence will be noticed, owing to gases being evolved; hold in the mouth of the tube a glass rod freshly dipped into lime-water; the drop of lime-water hanging upon its end will become milky, showing that carbon dioxide is one of the gases evolved. Hold a burning taper to the mouth of the test-tube; a blue flame will be seen, caused by the carbon monoxide gas burning in the air.

<sup>1</sup> Strong sulphuric acid is a very corrosive liquid, and great care must be taken not to get any upon the skin or clothes; should any of this acid or of any other acid get upon the skin it must be at once washed off; if it should accidentally be spilt upon the clothes, the part must be rubbed with ammonia solution. If the acid has remained for some time on the clothes it will produce a red stain, which will be removed by ammonia solution, unless it has been caused by nitric acid.

In order to get rid of the carbon dioxide gas which is mixed with the carbon monoxide, the mixed gases are "washed" with solution of caustic soda, or passed over pieces of solid caustic soda; the soda absorbs the carbon dioxide readily, but allows the carbon monoxide to pass on:



Exp. 27.—Heat the mixture of oxalic acid and strong sulphuric acid in a flask (A) fitted as shown in Fig. 10, and pass the gases either into a wash-bottle (a small Woulffé's bottle, or a broad-necked bottle), fitted as shown in B, and containing caustic soda solution; or through a tube (a) containing fragments of quicklime, or a U-tube (b) filled with fragments of caustic soda or soda-lime or with fragments of pumice-stone or broken tobacco-pipe stem

FIG. 10.

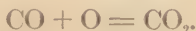


moistened with strong caustic soda solution. If the carbon dioxide is to be completely removed, the gases must be passed through two or more such tubes or bottles. The carbon monoxide gas thus more or less perfectly freed from carbon dioxide may be collected over water, and will be found to give either no milkiness with lime-water or a slight milkiness if the stream of gas has been so rapid that the caustic soda has not been able to absorb the carbon dioxide completely. By heating a formate with strong sulphuric acid carbon monoxide alone is given off, and is thus readily obtained free from carbon dioxide.

Carbon monoxide resembles hydrogen in being inflam-

mable and in extinguishing a burning taper; it also explodes when mixed with oxygen or air, hence before collecting a cylinder of the gas for experiment, ascertain that the gas coming off from the apparatus is free from air by collecting a small test-tube full and proving that it burns quietly.

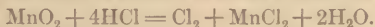
EXP. 28.—Push a burning taper up into a cylinder filled with carbon monoxide; the gas will burn with a blue flame at the mouth of the jar but the taper will be extinguished. As soon as the gas has ceased to burn inside the cylinder, pour in a little lime-water and shake it about; the liquid becomes milky, showing that by the combustion of carbon monoxide in the oxygen of the air carbon dioxide gas is produced:



*Tests for Carbon Monoxide.*—Carbon monoxide is recognized by burning with a pale-blue flame in the air, producing carbon dioxide, which renders lime-water milky.

V. *a.* *Chlorine gas* may be made in the apparatus employed for the preparation of carbon monoxide. The washing-bottle may either be dispensed with or may be used containing a little water to free the chlorine from hydrochloric acid gas.

EXP. 29.—Place some manganic oxide powdered, or better in small lumps, in the flask A (Fig. 10, p. 38), pour upon it some strong hydrochloric acid, mixed with about one-third its measure of water, and heat gently in a draught-cupboard or in the open air. A greenish-yellow gas is evolved, which may be collected by displacement, like carbon dioxide, since it is much heavier than air:



The gas has a very destructive action on the lungs, and must on no account be inhaled; it is usually recognized by its yellowish-green color, its peculiar smell, and by its property of bleaching moist vegetable colors. This last property is shown by placing in a jar of the gas a piece of moistened litmus-paper or fabric dyed with madder ("Turkey red"). The colors of both will be destroyed. A burning wax taper plunged into a jar containing chlorine continues to burn with a very smoky flame. Oil of turpentine, introduced into the gas by moistening a strip of filter-paper with the warm liquid, catches fire of itself and gives rise to dense smoke. A piece of dutch-foil or copper-leaf also burns when dropped into chlorine.

*Tests for Chlorine.*—Chlorine gas is recognized by its yellow color, its smell, and its power of bleaching moistened litmus-paper.

• V. b. *Hydrogen chloride, or hydrochloric acid gas.*

EXP. 30. —Place in the cleansed flask *A* (Fig. 10), which was used for the preparation of carbon monoxide, some lumps of sodium chloride (common salt) obtained by breaking up a mass of melted table salt, or by breaking a piece of rock-salt; pour upon it strong sulphuric acid and heat gently. Hydrochloric acid gas is evolved:



and being heavier than air may be collected by displacement, in the same way as carbon dioxide. The gas fumes strongly in moist air, turns moistened blue litmus-paper red, dissolves easily in water (EXP. 24), giving an "acid" liquid (hydrochloric acid), which, like the gas, turns blue litmus red.

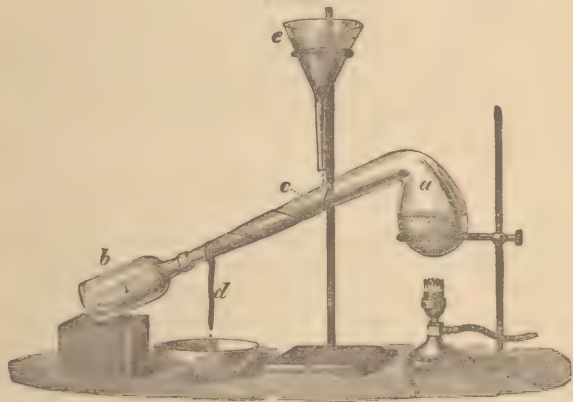
*Tests for Hydrochloric Acid.*—This gas is known by fuming in the air, turning moistened blue litmus-paper red, giving white fumes with ammonia gas, and yielding when dissolved in water a milky liquid on addition of silver nitrate solution, which does not become clear on adding nitric acid.

VI. DISTILLATION.—This process is employed to separate liquids which boil at a comparatively low temperature, either from solids, or from other liquids which are not converted into vapor at all or only at much higher temperatures. It consists in boiling the liquid and cooling or "condensing" the vapor, which is thus given off, again into a liquid—the "distillate;" the non-volatile solid or liquid substances present are thus left behind in the vessel in which the liquid is boiled. As examples of this process, the purification of common spring-water from the solid substances dissolved in it, and the preparation of nitric acid, may be performed.

EXP. 31. *Distillation of Water.*—Pour into a clean retort, *a* (Fig. 11), some tap-water through a funnel placed in the mouth, or in the "tubulure" (*i. e.*, the opening for the stopper or cork) if a tubulated retort is employed. Support the retort, whose bulb has been about half filled with water, in a retort-stand or upon a tripod, with its neck sloping downwards and dipping into a small clean flask or bottle, *b*, which is partly immersed in cold water contained in an evaporating basin. Cover the bulb of the flask with a broad strip of filter-paper, whose ends dip into the water contained in the dish; or, instead of cooling the flask cool the neck of the retort, by wrapping

round the lower part of it a piece of filter-paper, *c*, and round this a piece of wet string or tow, *d*; then arrange a funnel, *e*, with its mouth partly stopped so as to drop cold water on the upper part of the filter-paper; this water will be drained off by the string, *d*, and must not be allowed to run into *b*. On carefully boiling the water in the retort steam passes into the flask and is there condensed to "distilled water." The first few drops should be thrown away, as they are apt to be impure from rinsing the retort neck and flask. Whilst this process of distillation is going on, add to some tap-water, contained in a test-tube, several drops of nitric acid and

FIG. 11.



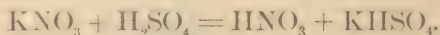
some silver nitrate solution, and notice that the water becomes milky. A separate portion in another test-tube will also be found to become milky on addition of some ammonia and ammonium oxalate solution. These changes are due to the presence in the water of certain solid substances dissolved in it. If the distilled water from the flask be examined in the same way it will remain clear, showing that these substances have been removed by distillation.

*Tests for Distilled Water.*—Good distilled water should remain quite clear when to separate portions of it are



added solutions of ammonium oxalate, silver nitrate, barium chloride, and ammonium sulphide; these tests prove the absence of calcium, chlorides, sulphates, lead, and iron respectively. It should also leave no residue when evaporated.

EXP. 32.—*Nitric Acid*.—Clean the retort from Exp. 31 by rinsing out the bulb with a little dilute hydrochloric acid, and then thoroughly with water; let it drain for a few minutes, and place in it some solid potassium nitrate (nitre); then pour upon this, through a funnel placed in the neck or tubulure, a quantity of strong sulphuric acid about equal in weight to the nitre used, and allow the acid to drain off the neck, in case a non-tubulated retort is employed, by supporting it for some time in an upright position. Proceed to distil just as in the preceding experiment; a yellow oily liquid will trickle down the neck of the retort into the flask; this liquid is somewhat impure nitric acid, and will be found to fume strongly in the air:



*Test for Nitric Acid*.—Place some small pieces of copper in a test-tube, pour upon them a little of this nitric acid; on warming gently reddish-brown fumes will appear in the tube, and a blue solution will remain (see Exp. 22, p. 34). This property of giving red fumes when treated with copper is often used as a test for nitric acid.

## SECTION II.

### PREPARATION AND USE OF APPARATUS REQUIRED IN ANALYSIS.

*Notes.*—Refer to the list in paragraph (494)<sup>1</sup>, which shows what apparatus is required for each student, and mark all apparatus as directed in the note at the end of the list.

1. *The Bunsen Burner.*—By far the most useful lamp for general heating purposes is the Bunsen burner (Fig. 12). It is a gas lamp so constructed that coal-gas entering through the tube *a* is mixed with a proper proportion of air which flows in through the holes at the foot of the burner, and the mixture of gas and air is burnt at the top of tube *b*. The oxygen of the air, which is thus mixed with the gas, burns the carbon in the interior of the flame. Accordingly the luminosity, which is believed to depend upon the existence in the flame of unburnt carbon or carbon compounds, is destroyed. The Bunsen flame is therefore useful because it deposits no soot upon a cool object which is being heated in it, and also because it is much hotter, owing to the more complete combustion of the gas, than any of the ordinary flames. Its high temperature, non-luminosity, and colorless appearance also render it very valuable for producing flame colorations, as will be seen hereafter. The lamp should be provided with some means for partly or entirely closing the air-holes when requisite; this is usually effected either by a loose perforated ring which is slipped over them, or by making the tube *b* turn round on its long axis. When a small



<sup>1</sup> Numbers occurring in the text which are inclosed in brackets refer to the paragraphs commencing in this section. For convenience in reference, paragraph numbers are printed in thick type; and at the head of each page the numbers of the paragraphs it contains will be found inclosed in square brackets.

flame is being employed, the air must be partly shut off, else the flame "burns below."

When the lamp is to be used, a piece of tightly fitting india-rubber tubing  $\frac{5}{16}$ ths of an inch in diameter is pushed over the end of the tube *a*, and the other end of the tubing is slipped over the tube which supplies gas to the working bench, the gas tap is turned on, and as soon as the gas is distinctly smelt issuing from the tube *b*, it is lighted. The flame should be almost perfectly colorless, and give scarcely any light. Occasionally the gas will burn at the bottom instead of the top of the tube *b*; this usually happens when the flame is turned down very low, or the supply of gas is insufficient; also when the quantity of air admitted through the holes is too great, or the burner is lighted too soon after turning on the gas tap. It may be at once detected by looking through the holes in the base of the lamp, when the luminous flame will be seen burning from the small gas-jet inside; the flame produced whilst the gas is "burning below" is also characterized by being long and somewhat luminous, and by emitting a very unpleasant smell. In such a case the flame should be at once extinguished by pinching the india-rubber tubing close to the burner, and the gas should be relighted after escaping for a few seconds. The momentary stoppage of the gas stream by suddenly striking the india-rubber tube upon the bench with the hand will also frequently cause the flame to rise to the top of the burner without extinguishing it. Closure of the air-holes serves the same purpose, but this must be done with care, as after the flame has burned below for a short time the metal becomes too hot to be touched. The risk of the gas burning below is prevented by slipping upon the top of the burner a tightly fitting thimble, with a hole in its top somewhat less in diameter than that of the burner.

2. *For diffusing heat over a large surface, the "rose burner" is very useful; it is a small perforated metal cap *c* (Fig. 12), which, when placed upon the top of the tube *b*, yields a small circle of flames; the rose burner is put on and removed by grasping it with crucible tongs;*

it is of course very hot after being removed, and should never be handled, or placed upon wood, until it is cool.

3. *The flame of a spirit-lamp* is occasionally employed instead of the Bunsen flame, but for general purposes the spirit-lamp should only replace the Bunsen burner where coal-gas cannot be obtained.

The spirit-lamp (Fig. 13) consists of a glass vessel containing methylated spirit, into which dips a cotton wick, supported by means of a brass or, better, a stoneware wick holder. When not in use the wick should be always covered with the glass cap to prevent evaporation of the spirit. If the spirit is tolerably free from resinous matter its flame will be non-luminous, and will deposit no soot upon a cold object.



FIG. 13.

4. *The blowpipe* is frequently used to produce a small but very hot flame from the flame of a gas-lamp, spirit-lamp, or candle, by blowing through it a fine stream of air from the mouth.

In order to obtain the "blowpipe flame" from the flame of a Bunsen burner, the blowpipe is held by the right hand, with its finely pierced tip *a* (Fig. 14) resting on the edge of the burner, and just inside the flame (Fig. 15); the mouth-piece *b* is then taken between the lips, and after blowing out the cheeks to their full extent, the air contained in them is forced out through the jet *a*, and causes a small pointed tongue of flame to issue from the side of the gas flame. The chief difficulty in learning to use the blowpipe properly is experienced in acquiring

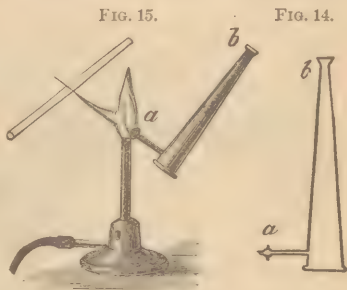


FIG. 15.

FIG. 14.

the habit of keeping up the blast of air for some time uninterrupted by the breathing. A little patient trial will, however, soon remove this difficulty, if it is borne in mind that the cheeks must be kept constantly inflated with air, and that the air must be forced through the blowpipe *by the pressure of the cheeks alone, and not by the action of the lungs*, breathing being carried on meanwhile through the nose, and the mouth being occasionally replenished with air from the throat just before breathing out the air from the lungs through the nose.

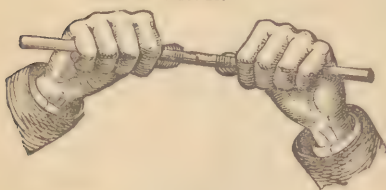
It is frequently necessary to have both hands free whilst using the blowpipe; this may be secured by resting the jet *a* on the top of the burner, and supporting the other end, *b*, by the lips alone, as shown in Fig. 15; or the blowpipe may be rested on a support of convenient height, such as the ring of a retort-stand properly adjusted.

The bright flame obtained by nearly closing the air-holes of the burner is much better suited for use with the blowpipe than the ordinary non-luminous flame. A burner with an elliptical orifice which gives a flat flame is commonly substituted for the ordinary round flame of the Bunsen burner; it is easily obtained by slipping a brass tube down the tube of the burner.

A further account of the uses of the blowpipe is given in par. 30.

5. *Glass tube or rod is cut* by laying it upon a flat surface, and making a

FIG. 16.



deep scratch with the edge of a three-cornered file at the point to be cut. The glass is then held with both hands, one on either side of the scratch and close to it, and a

gentle pressure is exerted upon the glass as if trying to break it across (Fig. 16). If the file-mark has been made sufficiently deep, the glass will readily break at the scratch; the sharp edges of a rod or tube should always be at once rounded by holding them in the Bunsen or blowpipe flame



until they are partly melted, or by rubbing them with the face of a file.

6. *Glass tube is bent* by holding the part to be bent in the upper edge of a common fish-tail gas flame, so as to heat at least two inches of the glass (Fig. 17). The Bunsen flame must never be employed for bending glass tubing; it produces a most unsatisfactory bend. The tube is supported by holding it with both hands, one on either side of the flame, and whilst being heated it is constantly turned slowly round on its axis so as to heat all sides equally. As soon as the glass is felt to be soft and pliable it is taken out of the flame and quickly bent to the required angle. The heated part must not be allowed to touch anything until it is cold; the soot is then removed from it by a cloth or piece of paper. A bend, if properly made, should be a curve, and should not alter the bore of the tube (Fig. 17 a); if a sharp angle is made the bore will be narrowed, and the bend, besides being unsightly, is very liable to break under a small strain (Fig. 17 b).

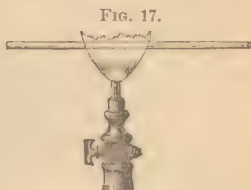


FIG. 17 a.

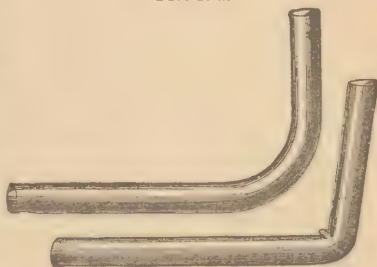


FIG. 17 b.

*Glass rod* may be bent in the Bunsen or blowpipe flame.

7. *Glass tube is drawn out* by holding it with both hands as for bending; and, whilst turning it constantly round on its long axis, the part to be drawn out is strongly heated in the Bunsen or, better, in the blowpipe flame (see Fig. 15); when the glass is well softened, the two ends are slowly pulled asunder in opposite directions.

8. *Corks are bored* usually by means of brass cork-borers, which are used as punches. A borer is selected of the same size as the glass tube which is to be inserted

into the cork, rather less than greater; the cork is then pressed against a wooden surface (best against the upright

FIG. 18.



edge of a thick bench or table), and the perforation made in it by gently pushing the borer through whilst constantly turning it upon its axis (Fig. 18). Caution and practice will enable the student to make

a clean straight hole without damaging the surrounding parts of the cork. In boring a single hole through a cork the easiest way to make it straight is to bore from the centre of one end halfway towards the other, then reverse the cork and bore a hole to meet this from the centre of the opposite end.

A perforation may also be made by pushing a sharply pointed round file carefully through the cork.

The round file is required for smoothing the interior of holes made by the cork-borer, or for slightly enlarging them when they are too small; whilst doing this great care must be taken to leave the hole round in shape, and not to enlarge it so much that the glass tubing when inserted fits loosely.

In perforating india-rubber stoppers the borer used must be sharp, and must be kept well wetted with water, or better with solution of caustic soda or potash.

The edge of the cork-borer is sharpened when necessary by rubbing the outer part of the edge obliquely with the face of a fine-toothed three-cornered or flat file.

9. *Sulphuretted Hydrogen Tube*.—A tube of the requisite shape will have been used for the experiments in Section I; it is seen as a bent delivery-tube in Fig. 5 (p. 30).

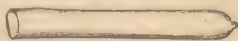
If not already made bend a piece of glass tubing (6) ten or twelve inches in length at right angles into the shape shown in Fig. 17 *a*, the shorter limb being about two inches long. This tube is to be kept for passing sulphuretted hydrogen gas through liquids.

10. *Small Ignition-tubes.*—A piece of hard glass tubing,<sup>1</sup> perfectly dry inside and out, and not much less than the eighth of an inch in internal diameter, is drawn out at its middle point by heating it strongly in the blowpipe flame, as shown in Fig. 15, p. 45. The narrowed portion of the tube (Fig. 19) is then cut across (5) at its middle

FIG. 19.

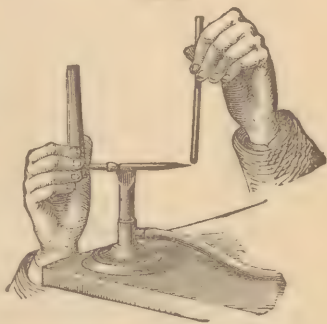


point, and by heating the conical part *a*, the narrow tube may be drawn off and a small closed tube is obtained (Fig. 19 *a*). If the closed end is strongly heated in the blowpipe flame and blown into whilst hot, it may be expanded into a small bulb, such as that seen in Fig. 36. Small test-tubes, three inches long by half an inch in diameter, serve well for ignition-tubes.

FIG. 19 *a*.

11. *Glass Stirring-rods.*—Three or four glass rods are made by cutting (5) a length of solid glass rod into pieces, some about seven inches long, others of about half that length. Any small projections are filed or chipped off, and both ends of each rod are then rounded by holding them in the upper part of the Bunsen flame, or better in the tip of the blowpipe flame, and turning the rod constantly round on its long axis until it becomes red-hot at the end (see Fig. 20); the sharp edges are thus partially melted.

FIG. 20.



<sup>1</sup> To distinguish hard glass from soft (lead) glass, hold the tube towards the light with one end near the eye; with hard glass the ring of glass will appear green or colorless, with soft glass black or dark.

The end of the rod must not be allowed to touch anything until it is cool.

**11 a.** Sometimes a very thin glass rod is required; this may be made from a stouter rod by softening it in the blowpipe flame (Fig. 15, p. 45), and then drawing it out until the required fineness is produced.

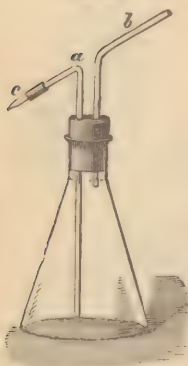
**12. Mounted Platinum Wires.**—The platinum wire used must not persistently color the flame green. Draw

FIG. 21.



out a piece of glass tube, six or seven inches in length, at its middle point (Fig. 15, p. 45) into the shape shown in Fig. 19. Cut it across at the middle of the narrow portion. Each piece of glass thus obtained serves for the handle to a wire. Break off the narrow part of the tube until it extends only about a quarter of an inch from the shoulder (a, Fig. 19), and into the narrow opening insert the end of a piece of platinum wire about two inches in length and bent round at its other end into a circle about

FIG. 22.



the eighth of an inch across by rolling it round a piece of thick wire; then hold the end of the wire surrounded by glass in the Bunsen or blowpipe flame until the glass melts and thickens around it, fixing it firmly when cold (Fig. 21). At least two wires should be mounted in this way. They are then rendered less liable to be lost and much more easy to handle. The wire may also be mounted by softening the end of a short piece of glass rod in the blowpipe flame, and sticking the wire into it.

**13. Wash-bottle.**—A thin flat-bottomed flask is chosen, best of the triangular shape shown in Fig. 22, and of 16 or 18 ounces capacity; the neck must not be less than an inch in

diameter. Procure a sound cork which is slightly too large to enter the neck, soften the cork by placing it upon the floor and rolling it backwards and forwards under the foot with gentle pressure; when thus softened the cork must fit tightly into the flask. A vulcanized india-rubber stopper is much more durable for this and most other chemical purposes; it is perforated by a sharp well-wetted cork-borer, or by a wetted round file. Two pieces of glass tubing rather longer than would be required for the tubes *a* and *b* are then bent (6) into the form shown in Fig. 22. The ends of the tubes are, if necessary, cut off to the right length, and their sharp edges are rounded by holding them in the Bunsen flame or in the tip of the blowpipe flame, or by rubbing them with the face of the file.

Two parallel holes are then bored in the cork by means of a round file or with a proper-sized cork-borer (8); the holes must be somewhat smaller than the glass tubes, and must not run into one another or to the outside of the cork. They are slightly enlarged, if necessary, by the round file. Into these holes the tubes *a* and *b* are then gently pushed with a twisting motion; if the holes have been made of the proper size the tubes must enter somewhat stiffly, but without requiring much pressure. If the holes have been carelessly made too large, the tubes may often be made to fit by slipping upon them little pieces of narrow india-rubber tubing, or by putting the pieces of india-rubber tubing into the holes in the cork before fitting in the glass tubes.

Upon the upper end of *a* is fitted a piece of small india-rubber tubing about an inch in length, into the other end of which is pushed a short jet (*c*) made by drawing out a piece of glass tubing in the flame (Fig. 15, p. 45); its opening may be contracted, if necessary, by holding it *perfectly dry* in the flame for a short time. The neck of the flask should then be bound round with twine like the handle of a cricket bat, or tightly covered with a piece of flannel; this prevents the fingers from being burnt when water has been boiled in the flask and its neck has become heated by the steam.



The wash-bottle, when thus fitted up, is filled about two-thirds with distilled water. Tap-water should never be kept in the wash-bottle.

A fine stream of water may then be obtained from the jet (*c*) by blowing down the tube (*b*); this stream serves for washing precipitates and for other purposes. A larger stream is obtained by inverting the bottle, when the water will flow out from the end of the tube (*b*), air entering meanwhile by the tube (*a*).

Hot water is frequently required for washing precipitates; to obtain this the wash-bottle is placed upon a piece of wire gauze supported on a tripod-stand, and is heated by the Bunsen flame, as shown in Fig. 10 (p. 38).

**14. Cleaning Apparatus.**—It is indispensable to the success of an analyst that all glass and porcelain apparatus should be scrupulously clean before being used.

Test-tubes, beakers, and porcelain dishes are washed in a stream of tap-water by using the test-tube cleaner (Fig. 23 *b*). A little hot hydrochloric acid will remove most stains, but occasionally it is necessary to heat a little strong sulphuric or nitric acid in a vessel in order to

FIG. 23.



cleanse it; hot caustic potash or ammonia solution may also often be used with advantage to remove grease. In fact, in removing a substance from a vessel to which it strongly adheres, the student should always consider what the substance is, and then remove it by a liquid in which it is easily soluble. Each article after having been well washed and rinsed with tap-water should be placed upside down in the small wicker-basket to drain, or if required for immediate use it should be rinsed out with a little distilled water. It should be borne in

mind that apparatus must be washed as soon as possible after use, as after standing the surface is usually much more difficult to cleanse. The brush must be cautiously moved as it reaches the bottom of a test-tube, since the glass is very thin and the brush is easily pushed through it.

**Test-tube Brush.**—It will be found that the piece of sponge at the end of the test-tube cleaner (Fig. 23 *a*) is

not well adapted to cleanse the bottom of test-tubes and boiling-tubes. A much more efficient end is given to the brush by removing the sponge and bending back the end of the wire stem upon itself at a point just above where the hairs commence (Fig. 23 *b*). By slightly curving the part of the stem carrying hairs, the brush will better adapt itself to curved surfaces such as those of porcelain dishes.

*Test-tubes* whilst in use are placed in the test-tube stand; boiling-tubes may be supported in the wicker-basket, or in a specially made stand. When washed they should be placed to drain mouth downwards in the wicker-basket.

*Glass funnels* should have their narrow stems cut off to within about half an inch from the shoulder; the sharp outer edge must then be removed by rubbing it with the face of a triangular file. The inside of the narrow neck is best cleaned by washing it with a common tobacco-pipe cleaner, inserted from the shoulder of the funnel so as not to cut the hairs by the edge at the other end of the neck.

15. *Platinum foil and wire are cleansed* by boiling them in hydrochloric acid and rinsing off the acid with water; the wire should then be strongly heated for some time in the blowpipe flame until, on being dipped into pure strong hydrochloric acid, it no longer colors the Bunsen flame. If the tip of the wire cannot be thus cleansed it should be cut off.

Commercial platinum often contains barium, and the wire made from it therefore gives a green color to the flame; such wire is useless for flame coloration tests and for spectrum analysis.

It is best to keep the foil or wire in a small beaker or dish containing strong hydrochloric acid diluted with sufficient water to prevent it from fuming; the platinum will thus be ready for use after having been rinsed with water.

16. *Before putting by apparatus* it should be made a rule to wash all glass and porcelain which is not in actual use, and place it in the wicker-basket to drain; the basket is put away with its contents.

All iron apparatus should be carefully dried, and must be kept in a dry place to prevent rusting. *On no account must metal apparatus be kept in the wicker draining-basket.*

17. *Heating Glass and Porcelain.*—A few general precautions should be observed in heating glass and porcelain vessels, to guard against cracking them.

A vessel containing a liquid must never be heated by the flame above the level of the liquid inside.

A dry hot vessel must be allowed to cool before pouring in any liquid, or placing it on a cold surface. See also (18, 19).

18. *Porcelain dishes* are generally used for boiling liquids; they are supported on a tripod or retort stand, and may be safely heated by the naked flame. *Porcelain crucibles* are used for containing solid bodies which are to be strongly heated; they are supported on a pipe-clay triangle placed upon the ring of a retort-stand or upon a tripod-stand: the flame should not be allowed to play steadily at once upon the bottom of the crucible so as to heat it suddenly, but should be constantly shifted by moving the burner, until the porcelain is hot. The crucible should also be allowed to cool slowly on the triangle, as contact with a cold body is very apt to crack it; the crucible and its cover whilst hot are handled by the crucible tongs.

19. *Glass vessels require to be heated* more cautiously than porcelain; a large naked flame must never be allowed to play for any length of time on any one part of the glass surface. In heating a test-tube or boiling-tube, this "local heating" is prevented by holding the tube obliquely with the lower part in the flame (Fig. 1), and moving it gently up and down, or by constantly turning it round on its axis. Test-tubes are too narrow for *boiling* liquids, in the liquid being very apt to boil over. *Small* quantities may be boiled and larger quantities heated short of boiling in a test-tube, but the broader "boiling-tubes" are best suited for this purpose. Large glass flasks, such as the wash-bottle, are most safely heated by placing them on a piece of wire gauze on a tripod-stand (Fig. 10, p. 38) and heating with a rose burner;

in some laboratories a sand-bath is available; the flask is then heated by being placed on the surface of hot sand. Test-tubes, if not full of liquid, can be held by the neck whilst being heated, if the tube be held obliquely so that the fingers are not over the flame. All risk of burning the fingers is avoided by bending round the neck of the tube a slip of folded paper or of leather, and pinching the ends together close to the tube.

## SECTION III.

### ANALYTICAL OPERATIONS.

THE student, before commencing the analytical reactions, must become familiar with the operations which are constantly employed in analytical chemistry. The processes will be most readily and perfectly understood by reading the following descriptions, and performing the experiments given in illustration of them.

**20. Solution.**—Many solid substances, if stirred or shaken with water, gradually “dissolve” in that liquid; salt and alum may be mentioned as examples. Other liquids may be employed instead of water, and if they cause the solid substance immersed in them to become partially or entirely liquid and mingle uniformly with the liquid, they are said to “dissolve” the solid, the liquid thus obtained being called a “solution” of the solid, and the liquid which dissolves the solid being termed the “solvent.” Thus water, when shaken with sodium chloride (common salt), dissolves it, yielding solution of sodium chloride; and water is therefore called a solvent for sodium chloride. Further, a solid which dissolves in a liquid is said to be “soluble” in that liquid; if it does not dissolve it is said to be “insoluble.”

The process of solution is more rapid when the solid substance is employed in the state of powder than when it is in large lumps, since a larger surface of the substance is exposed to the solvent by the powder; it is also much hastened by heating the solvent, which causes a more rapid circulation of the liquid over the solid, and also frequently increases the solubility of the substance.

Two kinds of solution may be distinguished. “Simple solution” occurs when a substance dissolves in a liquid without alteration in composition, the solution possessing therefore the taste, color, and other general properties of



the solid, and yielding the solid substance again when the solvent is removed by "evaporation." Solution of sodium chloride in water is an example of a "simple solution."

"Chemical solution," on the other hand, is always attended by a chemical change in the substance to be dissolved; and since the solution therefore contains a substance differing in composition from the undissolved solid, the properties of the solution are usually not the same as those of the undissolved solid, and on removing the solvent by evaporation the original substance is not obtained.

In dissolving solid substances in liquids, test-tubes, porcelain basins, or small glass flasks are generally employed.

EXP. 33.—Place a piece of potassium nitrate (nitre) in a small clean beaker, fill the beaker one-third with water,<sup>1</sup> and stir the solid about in the water with a glass rod; the potassium nitrate will *slowly* dissolve in the water; if the liquid be heated the solution will be much more rapidly effected. Powder another piece of potassium nitrate by crushing it and then rubbing it in a mortar with the pestle; place this powder in a test-tube, pour in water, and heat the bottom of the test-tube; the potassium nitrate will dissolve much more rapidly than before, showing that solution is accelerated by powdering the solid and employing heat. Keep these solutions.

EXP. 34.—Powder a little copper sulphate (blue vitriol) in a mortar, place it in a small porcelain dish, half fill the dish with water, and heat it on a tripod or retort stand. The *blue* copper sulphate dissolves, yielding a *blue* solution. Keep this solution.

These two experiments are both examples of "simple solution." Exp. 33 shows that a colorless solid gives a colorless solution. Exp. 34 proves that a colored solid gives a colored solution. This is generally true, and hence we can often infer the presence or absence of a colored substance in a solution by merely noting the

<sup>1</sup> Here and in all subsequent cases *water* must be understood to signify *distilled water*.

color of the liquid. Moreover, if a drop of the potassium nitrate solution be tasted, it will be found to possess the same taste as the solid; chemists occasionally rely upon taste, as well as upon color, when examining "simple solutions."

EXP. 35.—Place in a test-tube a small piece of calcium carbonate (marble or chalk), pour upon it a little water, and heat the tube. The calcium carbonate will be found to be "insoluble" in water. Add to the water some hydrochloric acid: "effervescence," or escape of numerous small bubbles of gas, will occur; the piece of calcium carbonate will meanwhile slowly diminish in size, and will at last entirely disappear in the liquid if sufficient acid is added.

EXP. 36.—Place in a test-tube a small piece of copper; on warming this with a little water it remains undissolved, but on adding to the water some nitric acid and heating, the copper slowly dissolves, giving off red fumes, and will be entirely dissolved if sufficient nitric acid is employed.

Experiments 35 and 36 are examples of "chemical solution;" the calcium carbonate is changed by the hydrochloric acid into calcium chloride, and this substance, *not the calcium carbonate*, remains in solution. The copper is changed into copper nitrate, which is then dissolved by the water. It will be noticed that in both these cases a gas is given off; this is a very usual, but not a universal, effect during "chemical solution;" the distinguishing fact is that the solid substance which is to be dissolved has undergone a chemical change in the act of passing into solution.

21. *Evaporation*.—When it is wished to obtain a substance, which is dissolved in a liquid, in the solid condition, the liquid is boiled away as a vapor, or "evaporated;" the solid substance is then left behind in the vessel.

EXP. 37.—Pour the potassium nitrate solution from Exp. 33 into a porcelain evaporating-basin, place the basin on a tripod-stand, and boil it over the Bunsen flame until the water has been nearly boiled away; then

make the flame smaller and continue heating until the water has disappeared. The solid potassium nitrate is left in the dish.

In evaporating a solution, a small flame or a rose burner should always be used towards the end of the process, and the flame should be moved about, if necessary, else some of the substance will spirt out of the dish.

Often a part only of the liquid is evaporated for the purpose of "concentrating" the solution, *i. e.*, making it stronger by removing a portion of the solvent. A solution, when sufficiently concentrated, will often form "crystals" of the dissolved substance if allowed to stand till cold.

EXP. 37 *a*.—Concentrate the copper sulphate solution made in Exp. 34, and allow it to cool; if sufficient water has been evaporated it will form crystals. Keep the copper sulphate in the dish.

22. *Precipitation*.—Two perfectly clear and transparent solutions, on being mixed together, often become more or less turbid and opaque, owing to a solid insoluble substance being formed in the liquid. A solid substance so formed in a liquid is called a "precipitate."

EXP. 38.—Pour into a test-tube some barium chloride solution, and then some ammonium carbonate solution; a white precipitate is formed owing to the production of insoluble solid barium carbonate. Keep this test-tube with the precipitate.

In the above instance barium chloride and ammonium carbonate separately dissolve easily in water, but if their solutions are mixed they yield by a chemical change two different substances,—ammonium chloride and barium carbonate. The former of these dissolves in water, but the latter (like marble) is insoluble, and therefore remains free as a powder in the liquid.

Substances are very frequently removed or separated in analysis by causing them to form insoluble compounds or precipitates with other substances which are added for the purpose.

\*In producing a precipitate, care must be taken that

the two solutions are well mixed; this mixture may be effected by closing the mouth of the test-tube with the thumb and several times inverting it, or often by simply warming the bottom of the test-tube in the flame; mixture may also be effected by stirring with a glass rod, or by pouring the liquid from one vessel to another. The last three methods are to be used when the liquid present is corrosive, and therefore must not be allowed to touch the skin. A precipitate which does not form readily is often caused to appear more rapidly on thoroughly mixing or agitating the liquid by the above means, or by heating it.

Precipitates produced with different substances differ much in appearance and properties; hence a precipitate is frequently formed to show the presence of a substance or to separate one substance from another. Substances thus added to produce precipitates are called "reagents."

The appearance of a precipitate is usually described by its color and its condition: it is "flocculent" if it forms in flocklike masses, "crystalline" if in small particles which are seen to be crystals under a lens or microscope, "gelatinous" if jellylike, etc. A slight precipitate causes only a "turbidity" in a liquid.

The color of a precipitate or liquid is often invisible or falsified by gaslight; if the color is to be seen at night, it should be examined with the light produced by a piece of burning magnesium ribbon.

Occasionally solid substances are used to produce precipitates; thus one metal is not unfrequently precipitated from its solution by immersing in the liquid another metal.

Exp. 39.—Dip a clean penknife blade into some of the copper sulphate solution left from Exp. 37 a, to which a few drops of sulphuric acid have been added; after a short time the metal copper is precipitated from its solution and covers the iron as a red film.

**23. Filtration and Decantation.**—It is frequently necessary to separate a precipitate from the liquid in which it is suspended. This is effected either by filtration or decantation.

**23 a. Filtration** is performed by pouring the liquid

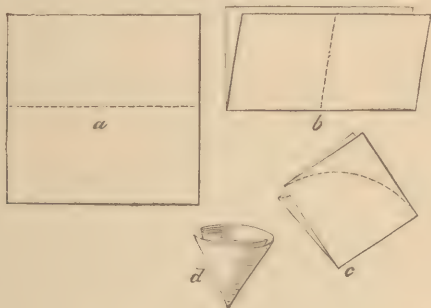
containing the precipitate upon some porous paper; the liquid itself runs through the pores of the paper, but the solid particles of the precipitate cannot pass through, and remain on the surface of the paper. The paper employed is called "filtering-paper," and the liquid which runs through is termed the "filtrate." A filtrate may frequently be colored by some substance *dissolved* in it, but it must always be perfectly clear and free from turbidity caused by solid particles *suspended* in it.

EXP. 40.—Measure a glass funnel from its shoulder to its edge along the sloping side (Fig. 24), cut a square of filter-paper whose edge is rather less than double this length, fold it across first along the dotted line (Fig. 25 *a*), then again as shown by the dotted line in Fig. 25 *b*. This gives a square (Fig. 26 *c*) which at one angle has four free corners; these are removed by cutting with a pair of scissors along the curved dotted line shown in Fig. 25 *c*. The "filter" is now made and merely requires to be opened; by separating the edges, formed by cutting off the corners, so that they form a circle, three remaining on one side of

FIG. 24.



FIG. 25.



the circle and one on the other, a little closed pointed paper bag is formed (Fig. 25 *d*); this is gently pressed *with dry fingers* into the *dry* funnel, and the folding altered if necessary till it fits tightly into the glass; it is



then moistened all over with a little water from the wash-bottle, and is ready for use.

The preliminary moistening of the filter-paper must not be neglected, since if the liquid and precipitate are poured upon a dry filter, some particles of the precipitate get between the fibres, which then swell by the wetting, inclosing the solid particles and stopping the pores of the filter.

As an example of the process of filtration, the barium carbonate precipitate obtained in Exp. 38 may be filtered off. Pour the liquid containing the precipitate upon the filter, the funnel being placed with its neck in a test-tube, and the test-tube being supported in a test-tube

FIG. 26.



stand (Fig. 26); care must be taken that the inside of the upper part of the test-tube is not wetted, else the space between the neck of the funnel and the inside of the tube is liable to become filled with liquid, and the egress of air being thus prevented the filtration is stopped. The funnel might also be supported upon the ring of a wooden filter-stand, and the filtrate be received in a small beaker in-

stead of in a test-tube. Take great care not to let the level of the liquid in the funnel reach the upper edge of the filter-paper. If the above directions have been carried out, and no hole has been made in the paper whilst preparing the filter, the filtrate will run through perfectly clear, leaving the barium carbonate on the filter. Keep the funnel, filter, and precipitate.

Circular filters can be purchased ready cut, and only requiring to be folded twice to be ready for use. The filter must always be of such size that when placed in the funnel its edge is below the rim. Sometimes the filtrate runs through turbid; it can then usually be made quite clear by passing the whole, or the first portions, of the filtrate once or twice again through the same filter; but with many precipitates a double filter should be used, a double filtration being thus performed in one operation.

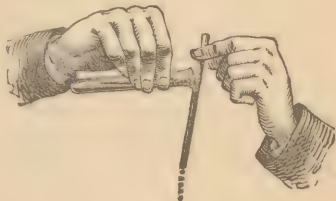
It should be borne in mind that hot liquids run through

a filter much more quickly than cold; hence, if not inadmissible for other reasons, a solution should always be boiled before being filtered.

*Note.*—Common filter-paper contains a little calcium carbonate, which is of no importance in ordinary analyses, and is only objectionable when a substance has to be examined for traces of calcium. To remove this impurity, in special analyses, the filters are moistened in a funnel with dilute hydrochloric acid, and then well washed with distilled water.

**23 b. Decantation.**—Precipitates which settle rapidly and completely in the liquid in which they are formed may frequently be separated from that liquid without the use of a filter. The vessel is allowed to stand at rest until the precipitate has completely settled, and the liquid is then carefully poured off or “decanted,” by allowing it to run gently down a wetted glass rod which is pressed against the edge or lip of the vessel (Fig. 27), the precipitate being left in the vessel. This process, if carefully performed, effects a fair separation of heavy precipitates. The precipitate obtained by adding sulphuric acid to some boiling solution of barium chloride may be separated by decantation. Keep the precipitate in the test-tube.

FIG. 27.



**24. Washing Precipitates.**—A precipitate which has been filtered from the liquid in which it was suspended has often to be washed until it is perfectly free from the adhering liquid. This “washing” is performed as described under 24 a if the precipitate has been separated by filtration, and by 24 b if by decantation.

**24 a. Exp. 41.**—Support the funnel, which contains the filter and barium carbonate precipitate from experiment 40, with its neck in a beaker or flask, and blow in a fine stream of hot distilled water from the wash-bottle, so directed by moving the jet with the fingers as to stir up the precipitate well; in this way fill the filter to

within a short distance from its edge; let this water run through perfectly, then nearly fill the filter again in the manner just described; repeat this process two or three times, letting the liquid run through perfectly each time before putting in a fresh quantity; the water running through from the third or fourth washing will usually be quite tasteless, and the precipitate and filter will be freed from everything soluble in water. Boiling, or at least hot, water should always be used for washing purposes, as the process is thus rendered much more rapid.

**24 *b*.** *Washing by Decantation.*—Heavy precipitates, after having been separated from liquids by decantation, are washed also by the same process. The precipitate is shaken or stirred with distilled water, and allowed to settle; when the water has become quite clear it is poured off (Fig. 27). By several times repeating this washing process with addition of fresh portions of distilled water, the precipitate may be entirely freed from adhering solutions.

The precipitate of barium sulphate, remaining in the test-tube from the experiment at the end of 23 *b*, may be thus washed by decantation.

**25.** *Drying Precipitates.*—A precipitate is often required in a dry condition after it has been filtered off and washed. It is dried by placing the funnel in a hollow tin cone or cylinder, the filter-dryer (Fig. 28), and supporting this on a piece of wire gauze upon a tripod-stand over the flame of a rose burner turned very low; or the filter-dryer may be placed on a gently heated sand-bath. The funnel is thus heated by the current of hot air, and rapidly dries the filter and precipitate. Great care must be taken to regulate the heat and watch the process, so as not to char the filter.

FIG. 28.



A more rapid method of drying a precipitate, after it has drained for a time, consists in spreading the filter upon a piece of wire gauze supported on a tripod-stand; a small flame from a rose burner is then placed beneath

the gauze, and the filter carefully watched to avoid charring it.

A precipitate is partially dried by opening out the filter upon several dry filter-papers; this process may precede those already mentioned.

**26. Removing Precipitates from the Filter.**—When a small quantity of a moist precipitate has to be taken from a filter to test its behavior or closely examine its appearance, it is most readily removed by dipping the end of a glass rod into the precipitate; by touching a watch glass or the interior of a test-tube with the end of the rod, a small quantity of the precipitate is deposited for examination.

If the precipitate is to be removed from the filter as completely as possible, several methods are available; one or other must be chosen according as circumstances render it suitable.

*a.* The bottom of the filter may be pushed out through the neck of the funnel with a glass rod, which is small enough to pass easily through the neck (11 *a*), and the precipitate may then be washed down into a vessel beneath with a fine stream of water or other liquid from the wash-bottle.

*b.* Without breaking the filter the funnel may be held with its neck horizontal, and the rim just inside the edge of a porcelain dish (Fig. 29); the precipitate is then washed out by directing a fine stream of water from a wash-bottle against the sides of the filter.

*c.* The filter and precipitate are allowed to stand for some time, so as to drain off as much water as possible; the filter is then carefully taken out of the funnel, partially dried if necessary by laying it upon several folds of filter-paper, and after removing the portions of the paper which contain no precipitate, together with the empty fold,<sup>1</sup> it is spread out inside a porce-

FIG. 29.



<sup>1</sup> Filters may be made without this fold, by cutting one of the round papers (Fig. 25 *d*) through across one of the folded diameters,

lain dish; the liquid with which it is to be treated is poured upon it, and by shaking the dish so as to cause the liquid to move round and round, and occasionally carefully stirring the precipitate with a glass rod, the precipitate is washed off the paper without tearing the latter to pieces. The paper is then carefully removed by a glass rod.

*d.* If it is undesirable to add a liquid to the precipitate upon the filter, the filter and precipitate, after draining for a short time, are removed from the funnel; the filter is spread out upon a flat piece of glass and the precipitate carefully scraped off with a glass rod or a small spatula. If the precipitate is required dry, the filter, after removal from the funnel, may be carefully opened and spread upon several thickness of filter-paper to drain. When there is a large quantity of the precipitate a sufficient quantity may be removed on the end of a glass rod or spatula, without taking the filter out of the funnel. This method is usually the most imperfect, but is frequently the best for other reasons.

*e.* A precipitate has sometimes to be dissolved off the filter; the hot liquid used as a solvent may then be poured upon the precipitate; it will run through the filter into a vessel below, taking with it the precipitate in solution. The liquid, after it has run through, should be heated again, and once more poured upon the precipitate, if the latter is not entirely dissolved; this re-heating and returning of the liquid to the filter should be continued as long as anything is dissolved; any remaining portion of the precipitate must then be removed by a little fresh solvent.

*f.* A precipitate, if small in quantity, may also be rinsed off the filter with the liquid with which it is to be treated or dissolved. The funnel is placed with its neck in a test-tube, the liquid is poured into the filter from another test-tube, and the precipitate is quickly stirred up with the liquid with a glass rod thin enough to pass down

bringing the cut edges together, and sharply folding them over several times, pressing them with the nail; if properly made, such a filter is perfectly impervious to the precipitate.



through the neck of the funnel ; the bottom of the filter is then pushed out through the neck by the glass rod, and the liquid carrying most of the precipitate will run through ; if some of the precipitate remains on the filter, the same liquid is poured through the filter again into the other tube, and by thus pouring backwards from one tube to another all the precipitate may be removed.

*Note.*—The greater part of a precipitate may often be removed by a clean knife or spatula, and the remainder by some one of the foregoing methods.

EXP. 42.—Remove the precipitate of barium carbonate remaining from Exp. 41 from the filter by one of the above processes, using hydrochloric acid as a solvent for method *e*.

27. *Ignition.*—Solid substances occasionally require to be heated strongly or “ignited.” This process of ignition is employed with various objects.

1st. In order to see what effect strong heat has upon a substance, since by this means we can frequently detect its composition. For this purpose we use small tubes made from hard glass tubing (10), or small test-tubes.

EXP. 43.—Heat a little mercuric oxide in a small tube of hard glass ; after a short time minute shining drops of the metal mercury will be seen on the upper part of the tube ; if then a small splinter of wood with a spark at its end be held in the tube it will burst into flame. The behavior of this red powder on being “ignited,” therefore, shows it to contain the elements mercury and oxygen.

Substances are often heated on platinum foil with the same object. Thus a little charcoal powder when heated on platinum foil burns away.

2d. Ignition is also used as a means of separating from a solid mixture substances which are “volatile,” or which change entirely into vapor when heated ; these are driven off by heat from other substances which are “non-volatile,” or can be strongly heated without changing into vapor, and which therefore remain behind.

EXP. 44.—Heat a small piece of ammonium chloride on a strip of platinum foil held in the flame by crucible

tongs; the ammonium chloride being volatile will give off white fumes, which are best seen by removing it from the flame for an instant, and the solid substance will slowly disappear or "volatilize."

Heat in the same way a small piece of potassium chloride; this will melt, but will not disappear, since it is only slightly volatile. It will become solid again on cooling.

Hence, if from a mixture of ammonium chloride and potassium chloride the potassium chloride is to be obtained alone, the mixture would be strongly heated for some time, when the ammonium chloride would be removed as vapor, leaving the potassium chloride behind.

28. *Sublimation* is the process of heating solid substances and converting them into vapor, then cooling this vapor so as to "condense" it, or render it solid again. A volatile substance may thus be obtained free from other substances which are not volatile or only slightly so.

EXP. 45.—Heat a small piece of ammonium chloride in a tube of hard glass closed at one end and two or three inches in length; it changes into vapor, which again cools into solid ammonium chloride in the upper part of the tube. This is an example of the process called "sublimation," and the solid substance at the upper part of the tube is a "sublimate."

29. *Fusion*.—Substances are often melted or "fused" together to cause certain chemical changes to occur between them. Melting or "fusion" is performed sometimes on platinum foil, but often in porcelain or platinum crucibles. For fusion in a crucible an intense heat is often requisite; this may be obtained by using the blowpipe flame, but the Bunsen flame will usually suffice if the crucible be surrounded by the conical filter-dryer (Fig. 28, p. 64) which steadies the flame and increases the draught.

EXP. 46.—Place upon a slip of platinum foil a mixture of powdered sodium carbonate and potassium nitrate, then a very small quantity of manganese oxide; hold the foil with crucible tongs in the top of the Bunsen flame, or heat the under surface of the foil with the blowpipe

flame. The mass will melt or fuse; it is kept in a melted state for a short time and then allowed to cool, when a bluish-green mass is obtained. The production of this color is due to the presence of sodium manganate formed by the fusion; this color on fusion with sodium carbonate and potassium nitrate is produced only when manganese is present, and is therefore a test for that element.

**30. Use of the Blowpipe.**—The blowpipe is used, as has been already explained (4), to obtain an intensely hot flame which may be made to play in a convenient direction upon any substance to be heated; it is very useful for analytical purposes, since by its skilful use the composition of an unknown substance, when ascertained by other means, can usually be confirmed; and with many substances (especially minerals) a complete, or at any rate sufficient, analysis can be made by the blowpipe alone. The way in which the flame is obtained has been already explained (4).

In a well-formed blowpipe flame two parts may be distinguished: the “inner flame,” which is blue and pointed, and around and beyond this an almost colorless flame, “the outer flame.” The inner flame is often called the “reducing” or “deoxidizing flame,” because it separates or “reduces” metals from their oxides and compounds, and in general “deoxidizes” substances; the outer flame is also known as the “oxidizing flame,” because it changes metals into their oxides, and “oxidizes” many other substances. These two flames also produce other distinctive effects.

The “inner flame” is best obtained of large size by placing the tip of the blowpipe nozzle only in the very edge of the flame, or even just outside it; the “outer flame” is best obtained by putting the nozzle much further into the gas flame. It may also be noted that the “reducing flame” is furnished most readily by the luminous gas flame; the “oxidizing flame” is most easily and perfectly formed from a Bunsen flame which contains some air, and which is obtained by either leaving the air-holes at the foot of the burner entirely open or by only partially closing them.

There are several purposes for which the blowpipe is employed in analytical chemistry with which the student should become familiar; the following experiments will exemplify the most important of them.

31. EXP. 47.—*Borax Bead*.—Place a little borax, which has been finely powdered in a mortar, upon a watch glass; moisten the loop of a piece of mounted platinum wire (12) with water or in the mouth, and dip it into the powdered substance, then hold the loop with the adhering powder in the blowpipe flame until the borax melts; if this is insufficient when melted to form a bead which fills the loop, dip the loop with the melted substance upon it again into the powder,—more powder will adhere and may be melted in the flame; in this way powder is to be constantly added until when held in the flame a liquid drop or bead is produced which completely fills the loop. This bead must be perfectly colorless and transparent on cooling. Keep the bead on the wire.

If the melted bead easily drops from the wire, either the loop or the bead is too large and must be lessened in size. The most convenient-sized loop is one which is rather less than one-eighth of an inch across; it is best made by rolling the tip of the wire round a piece of stout wire. If the bead is too large, remove a portion whilst it is in a fused condition by giving the wire a sudden jerk.

Certain substances when melted in this bead color it, and as a rule the color produced by each of these substances has some characteristic tint or peculiarity. The color of the bead should be examined after it has been heated, first in the outer and then in the inner flame, and must be noted both hot and cold. If the bead appears opaque, on account of too much of the coloring substance having been introduced, it can generally be made transparent by shaking off some of the fused borax, or by flattening the fused bead by gently squeezing it between a small pair of pincers.

EXP. 48.—Moisten the clear cold borax bead and dip it into some powdered ferrous sulphate, thus taking up *very little* of the powder upon it; then heat the bead and substance for a short time in the tip of the outer blow-

pipe flame, and examine the color of the bead by looking through it at a piece of white paper or at a window light; it will be reddish-brown whilst hot, but the color will become lighter on cooling; now heat the bead again for some time in the tip of the inner blowpipe flame; its color will be changed to green. These two colors, shown by the borax bead in the outer and inner blowpipe flames respectively, characterize the metal iron.

The fused borax bead is detached by giving the wire a sudden jerk; it may also be removed after cooling by crushing it on a hard flat surface by a sharp blow with the pestle. The wire when not in use should be kept in dilute hydrochloric acid. Should it not be perfectly clean after washing off the acid, the simplest method of cleansing it is to make a fresh bead upon the loop and jerk it off whilst melted; this will usually remove all impurity. A borax bead must never be used for these purposes until it has been found to be perfectly colorless, both hot and cold, when heated in the outer blowpipe flame. If the first bead which is made in the loop is tinted with any color, it must be jerked off whilst fused and another bead formed with fresh borax, this being also thrown off and replaced if not quite free from color; this process is to be repeated until the bead is obtained perfectly clear and colorless.

**32. Flame Colorations.**<sup>1</sup>—Many substances give a characteristic color to the flame. The blowpipe flame is often employed to obtain these colors; an ordinary Bunsen flame, however, although it does not give the colors quite so promptly and intensely, answers the purpose well.

The flame best suited for this purpose is obtained by surrounding the Bunsen flame with a conical chimney, reaching about two-thirds of the height of the flame (Fig. 30), and then so regulating the supply of air entering into the air-holes that a small luminous point appears near the top



<sup>1</sup> For a more detailed and exact description of flame tests, see Bunsen's paper in the *Philosophical Magazine* for 1867.



of the flame; the platinum wire is held either in this luminous tip or just above it. A filter-dryer also forms a very good chimney, being supported just above the foot of the burner on a wire tripod, which may be made by bending down the ends of a pipe-clay triangle.

EXP. 49.—Hold a loop of platinum wire in the inner blowpipe flame; if the wire is clean it will become red-hot without coloring the flame. If it colors the flame, clean the wire by boiling it with hydrochloric acid in a test-tube, and then rinsing well with water; or by moistening with strong hydrochloric acid, and heating strongly in the blowpipe flame until it no longer colors the flame. If it cannot be thus cleansed, cut off the end. Now moisten the wire and dip it into a little powdered sodium chloride, or dip the loop into some sodium chloride dissolved in water, so that when removed a drop of the solution remains in the loop, then hold the loop at the tip of the inner blowpipe flame; the outer flame will be colored bright yellow. Repeat the experiment, placing the moistened loop in the upper and outer part of the Bunsen flame; the same yellow tint will be obtained. This yellow color is given only by sodium and its compounds.

Remove all sodium chloride from the platinum wire loop by heating it strongly in the tip of the blowpipe flame until it ceases to impart any color to the flame. Then dip the wire into some potassium nitrate solution; this will give to the flame a pale-violet color, which is characteristic of potassium and its compounds.

As will be seen subsequently, the examination of flame colorations, aided by the use of colored glasses, and of a hollow glass prism filled with indigo solution, is of great use in ordinary analysis.

EXP. 49 *a*.—Look at the yellow flame coloration produced by sodium chloride through a piece of cobalt glass or through the indigo prism; no yellow color will be visible. Now dip the wire loop into a mixture of a few drops of sodium chloride and potassium chloride solutions; when held in the flame only the sodium coloration is seen, but through the blue glass or prism the potassium is seen to produce a red flame coloration. By means

of the blue glass or prism then potassium is discoverable in the presence of sodium, by which its presence is otherwise masked.

By far the most perfect method of examining flame colorations, more especially for the rarer elements or for mere traces of the more common ones, is by the use of the spectroscope; every advanced student should make himself familiar with the use of this instrument, at least in its simplest and smallest form. A paper on the use of the spectroscope for qualitative analysis will be found in the appendix; this is well worthy of the attention of senior students.

Two platinum wires should be kept in readiness, one to be used for borax beads and the other for flame colorations, since a loop which has been used for borax colors the flame yellow.

**33.** *Ignition on Charcoal in the Blowpipe Flame.*—Wood charcoal forms a very useful support for substances which are to be heated in the blowpipe flame. It cannot itself be melted, it conducts heat very badly, and possesses other properties which render it peculiarly adapted for ignitions. It is, if necessary, sawn into small pieces of the required shape and size with a fine-toothed saw.

Ignition on charcoal serves chiefly to detect the presence of metals; the substance for this purpose is heated either alone or mixed with certain other substances (usually sodium carbonate and potassium cyanide) in the inner blowpipe flame; globules or scales of the metal are thus frequently produced, also in many cases the oxide of the metal forms a characteristic coating or "incrustation" on the charcoal; an examination of the color and properties of the metal or incrustation, or of both, will frequently lead to the detection, or confirm the presence, of some metal. Charcoal is apt to leave a white ash when heated alone in the blowpipe flame; this must not be mistaken for an incrustation. A powder frequently requires to be moistened with water before being heated by the blowpipe flame, in order to prevent the flame from blowing it off the charcoal.

EXP. 50.—Choose a piece of wood charcoal free from large cracks, scoop out a small hollow near one end with

FIG. 31.



a knife, and place in the hollow a small quantity of a mixture of powdered lead acetate and sodium carbonate or potassium oxalate. Heat this mixture in the inner blowpipe flame, holding the charcoal in such a way that the rest of the flame plays over its surface (Fig. 31). After heating for some time bright globules of lead

will be seen in the cavity, and on removing the charcoal from the flame the surface round the cavity will be found to be colored with a yellow "incrustation." If one of the little globules of metal be then taken off the charcoal with the point of a penknife, and be struck smartly with a pestle on the bottom of a mortar turned upside down, it will flatten out into a cake, showing that the metal is "malleable" not "brittle." The metal lead is the only metal which gives a yellow incrustation and malleable globules; this test therefore serves to detect its presence.

33 a. The melted mass left on the charcoal after fusing a metallic salt with sodium carbonate is best examined for metallic powder or scales by detaching it from the charcoal with the point of a penknife, then crushing it in an agate mortar or in a watch glass with a little water; on stirring and quickly decanting the water down a wet glass rod or pestle held against the edge of the vessel (Fig. 32), the metallic powder, if present, will be left; by repeating this process of "levigation," the metal is obtained free from soluble substances and charcoal; it may then be further examined by a lens or magnet. A mixture of copper sulphate with sodium carbonate, when heated on charcoal and "levigated" as directed above, will furnish little red scales of copper; a mixture of fer-

rous sulphate and sodium carbonate will yield a gray powder consisting of metallic iron, which, when touched with the point of a magnetized knife, will become attached to it.

FIG. 32.



**34. Use of Test-papers.**—Certain vegetable colors undergo remarkable changes when acted upon by chemical substances. Some of these are used for analytical purposes; the following experiment will explain how they are made use of.

**EXP. 51.**—Boil some pieces of a common red pickling cabbage-leaf in water; a blue liquid will be produced. Pour some of this liquid into a test-tube and add several drops of hydrochloric acid, the color will change to bright red; to another portion of the blue liquid add several drops of ammonia, the color changes to green; to a third portion of the blue liquid add a little ammonium chloride solution, the color remains unchanged.

Mix in a test-tube a little ammonia solution with three times as much distilled water, and add this weak ammonia gradually to the liquid reddened by several drops of hydrochloric acid; by careful addition the blue color may be exactly restored, the acid previously added being “neutralized” by the ammonia.

**EXP. 52.**—Pour some blue litmus solution (made by boiling solid litmus in water and filtering) into three test-tubes; to the first add hydrochloric acid drop by drop until it turns distinctly red, preserve this liquid; to the second add ammonia solution, the liquid remains blue; to the third add ammonium chloride solution, the color will not be affected.

Divide the reddened liquid into three parts; to one part add ammonia solution, the original blue color is restored; to another part add hydrochloric acid, the red color is unchanged; to the other part add ammonium chloride, the red color remains unaltered.

These experiments may also be made with litmus test-papers, which are prepared by soaking paper in the blue and red liquids respectively, and allowing it to dry.

Exp. 53.—Repeat the preceding experiment, using the litmus-papers instead of the solution, and moistening them with the liquid by dipping a glass rod into it and then touching the paper with the moistened end; the results mentioned in Exp. 52 will be obtained.

It will be seen then that the three substances employed differ in their action on litmus test-papers, as follows:

Hydrochloric acid.....	reddens	blue litmus	does not affect	red litmus.
Ammonia.....	does not affect	"	blues	"
Ammonium chloride...	"	"	does not affect	"

Each of these substances is a sample of a whole class, the members of which resemble it in their action on litmus.

The class of *acid substances*, including sulphuric acid, nitric acid, etc., and many metallic salts, resemble hydrochloric acid in reddening blue litmus and not affecting red.

The class of *alkaline substances*, including potassium hydrate, sodium hydrate, etc., and many salts of the alkalies, resemble ammonia in bluing red litmus and not affecting blue.

The class of *neutral substances*, including potassium chloride, sodium chloride, etc., resemble ammonium chloride in not affecting either blue or red litmus.

Hence in analysis we use red and blue litmus-papers to test whether a liquid is "acid," "alkaline," or "neutral."

The red cabbage liquid, as will be seen, is better suited for a test-paper than litmus, since one paper shows both



alkalies and acids; but the color is very apt to spoil with keeping.

Sometimes a liquid in which a colored precipitate is suspended has to be tested by litmus-paper; the precipitate then frequently hides the color of the paper when a drop of the liquid is placed upon it. In such a case moisten the paper with a drop of liquid, and wash the liquid off after a short time with a stream of distilled water from the wash-bottle; the color of the paper is then distinctly seen.

**35. Making Neutral, Acid, and Alkaline.**—An acid substance by being mixed with a proper proportion of an alkaline substance becomes “neutral;” similarly an alkaline substance is rendered “neutral” by mixture with a proper quantity of an acid. Thus by mixing hydrochloric acid and ammonia in the proper proportions, the neutral substance ammonium chloride is formed; the acid is then said to be “neutralized” by the alkali, or the alkali by the acid.

It is often required to “neutralize” an acid with an alkali or *vice versa*. The following experiment will show how this process of neutralizing an acid is performed.

**EXP. 54.**—Pour a little hydrochloric acid into a porcelain dish, add to it ammonia, several drops at a time, keeping the liquid constantly stirred with a glass rod, and occasionally touching a slip of blue litmus-paper with the end of the rod moistened by the well-stirred liquid; as soon as the paper is only faintly reddened by the liquid, the ammonia is added very carefully, stirring well after the addition of each drop, and trying the action of the liquid by touching the wet glass rod against first blue and then red litmus-paper, waiting a short time to give the liquid time to act on the paper. When the colors of both blue and red paper remain unaffected, the process of “neutralization” is completed.

It is well to add *dilute* ammonia towards the end of the process; this is prepared by mixing a little ammonia with three or four times as much distilled water in a test-tube.

The process of neutralizing may often be simplified, when the liquid is clear and colorless, by dropping into it a small piece of blue litmus-paper, the color of which is noted after each addition of ammonia; the condition of the liquid should, however, even in this case be proved towards the end by moistening with it both red and blue paper.

The process of neutralizing an alkali with an acid is precisely similar to that of neutralizing an acid with an alkali, except that red litmus is at first used instead of blue.

35 a. It will be readily understood from what has been said above, that if an alkaline or neutral liquid is to be "acidified," acid is added gradually, as was described in the preceding experiment, until a drop of the well-mixed liquid reddens blue litmus-paper. If an acid or neutral liquid has to be made alkaline, the alkali is added until a drop of the liquid turns red litmus blue. These processes are often termed adding acid or alkali "in excess."

35 b. *Yellow turmeric-paper* is occasionally employed instead of red litmus to test for alkalies, which turn it reddish-brown; it is unaffected by acids, with the exception of boracic acid. The most important use for turmeric-paper is to test for boracic acid, the solution of which, if dried on the paper at a gentle heat, turns it orange-red.

EXP. 55.—This may be shown by stirring a little borax upon a watch glass with dilute hydrochloric acid until it is dissolved, then moistening the lower part of a slip of turmeric-paper with this liquid, and holding it some distance above the flame, or, better, placing it in a steam oven until dry; the portion of the slip which was moistened will now appear reddish-brown, the color being well seen by contrast with the light-yellow upper portion of the paper.

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## FRACTIONAL SOLUTION, CRYSTALLIZATION, AND DISTILLATION.

1. *Fractional Solution*.—Since different substances show differences in solubility in water and acids, it is often possible by means of solvents to separate the constituents of a mixture. This process is termed separation by “fractional solution.” Illustrate this by making a mixture of powdered ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and ferric oxide ( $\text{Fe}_2\text{O}_3$ ); on warming a portion of this with water,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  alone dissolves, leaving  $\text{Fe}_2\text{O}_3$ : if another portion is warmed with  $\text{HCl}$ , both substances dissolve.

2. *Fractional Crystallization*.—If a solution of two different salts be boiled down in an evaporating basin, one salt will usually furnish crystals before the other does, and by this process of “fractional crystallization” a separation of the salts may often be effected. Boil down a solution of sodium chloride ( $\text{NaCl}$ ) and nitre ( $\text{KNO}_3$ ):  $\text{NaCl}$  will crystallize out of the boiling liquid in hollow cubes, and on cooling prisms of nitre will separate.

3. *Fractional Distillation*.—Liquids which boil at different temperatures may often be separated by distillation (p. 40); that part of the mixture which first distils over consisting chiefly of the liquid with the lowest boiling-point, and the successive portions of the distillate becoming richer in the liquids of higher boiling-points. The process of “fractional distillation” may be illustrated by distilling a mixture of alcohol and water; since alcohol boils at a lower temperature than water, the first part of the distillate contains the greater part of the alcohol, as is shown by its burning and by its dissolving camphor or iodine in quantity. The last portion of the distillate does not give these tests for alcohol, and is proved to be water by turning dry  $\text{CuSO}_4$  blue and dissolving it.

## SECTION IV.

### ANALYTICAL REACTIONS.

*Course of Practical Analysis to be Pursued by the Student.*—The text is so arranged that two main courses may be framed from it in this and the following sections. The one is suited to senior students, and dispenses with the training in the detection of simple substances, which, although useful as a stepping-stone to the full analytical method, is in itself of only small importance. The other course is suited to junior students, and forms an easy approach to the more difficult complete methods of analysis; it teaches the plan of analyzing simple substances which may contain one acid-radicle and one metallic-radicle. This course is therefore also suited to those who are learning analytical chemistry with the view of preparing themselves for examinations in which the candidate is not required to detect more than one acid-radicle and one metallic-radicle. These courses are described below as the “senior course” and “junior course.”

*The senior course* consists in working through the analytical reactions in Section IV; as those for each group are completed, several substances whose composition is unknown to the student are tested for one member only by the “table of differences” at the end of the group; as soon as these are detected with readiness, substances which may contain two or more of the members mixed together are analyzed by the group-table in Section VI: a reference to the “table of differences” will show at a glance on what principles these group-tables are founded, and this is further explained by a statement following the “table of differences.” This plan of working with each group-table before going on to the reactions for the next group is to be recommended, since, whilst the differ-

ences upon which the separation and special tests of the elements in the groups are fresh in the student's memory, they are practically applied. The analytical tables are thus gradually rendered intelligible one after another, whilst the student is proceeding through the reactions. The book is so arranged, however, that the analytical tables may be left until the reactions for all the groups have been finished. When all the groups have been worked through in this manner, the analysis of substances is commenced which may contain any members of any of the different analytical groups; the directions for the systematic method of analysis required for this purpose being contained in Section VI.

*The Junior Course.*—Since this is intended to teach only the detection of one metallic and one acid radicle, the student, whilst working through Section IV, omits all those paragraphs marked "s" after the number, relating to the separation and detection of the mixed members of a group; and, after finishing the reactions for each group, he proceeds to detect the members occurring singly in several substances of unknown composition by the table of differences, and by reference to the reactions. After working in this way through Section IV, he at once proceeds to analyze simple substances by Section V.

As stated above, this junior course may occasionally be made to precede the senior with advantage; that is to say, the student, after working through the junior course, and learning how to detect simple substances, may analyze mixtures containing two or more members of each group by the directions given at the end of each of the groups in Section IV, and may then proceed to the full method of analysis contained in Section VI.



## INTRODUCTORY REMARKS ON ANALYTICAL CHEMISTRY.

The science of chemistry reveals to us the fact that every substance on this earth, and probably in the universe, consists either of one kind of matter only, or of two or more different kinds which we cannot further separate. Those substances which contain only one kind of matter are called "chemical elements;" their number at present amounts to a little over sixty. A list of them is given in paragraph 558 at the end of the book.

It is not often that these elements occur singly; two or more of them are commonly found together either in a state of mere "mixture," or united in a much more intimate manner by the force of "chemical affinity" to form a "chemical compound."

Analytical chemistry or analysis (literally meaning an *unloosening* or *separation*) teaches us how to discover what element, elements, or sometimes what groups of elements, any substance of unknown composition contains; it also enables us to ascertain whether any particular element or group of elements is present in a given substance. In order to become a thorough analyst, it is necessary to be intimately acquainted with the properties of every element and of the compounds it forms with other elements, and therefore efficiency in analysis depends in a large measure upon the knowledge of what is usually termed "theoretical," or more appropriately, perhaps, "descriptive chemistry." But, although we recognize a substance by its properties, still a knowledge of *all* its properties is not requisite to enable us to detect its presence; for ordinary analytical purposes certain marked properties of each element or group of elements are selected, and by these properties, called "tests" or "reactions," we detect its presence.

The "tests" or "reactions" most frequently selected are the following: 1st. The behavior of a substance when heated under various conditions; and 2d. Its behavior when mixed with certain liquid or solid substances; such

substances, added for analytical purposes, are called *reagents*. Some reagents serve for detecting one element or compound only, and are therefore called *special reagents*; others separate or detect a group of elements or compounds, and are called *group reagents* or *general reagents*; these latter reagents serve to separate substances into "analytical groups," as will be more fully explained hereafter.

The student must bear in mind that, although an acquaintance with the most important reactions of substances is indispensable to success as an analyst, caution, skill, and neatness in manipulation are not less necessary, and the most scrupulous attention must be paid to all directions bearing on these matters.

**36. Analytical Classification.**—The chemical elements are frequently divided into two classes, viz., *metals* and *non-metals*. These classes form, with a slight modification, convenient divisions for analytical purposes. In the class of "metals" must be included the hypothetical metallic-radicle ammonium ( $\text{NH}_4$ ), also the element hydrogen. The class of "non-metals," either singly, or in groups formed by their combination *inter se* or less frequently with a metal, unite with hydrogen and with metals forming "salts;" the hydrogen salts of these radicles are usually called "acids." Thus  $\text{Cl}^1$ ,  $\text{SO}_4$ ,  $\text{PO}_4$ ,  $\text{MnO}_4$  form the hydrogen salts or acids,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HMnO}_4$ , and the metallic salts,  $\text{KCl}$ ,  $\text{MgSO}_4$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{KMnO}_4$ ; metal-hydrogen salts or acid salts, such as  $\text{NaHSO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , are also known. The general name, "acid-radicle," is conveniently applied to  $\text{Cl}$ ,  $\text{SO}_4$ ,  $\text{PO}_4$ ,  $\text{MnO}_4$ , etc., it being understood that although most of these are unisolated compound radicles,—*i. e.*, groups containing more than one element,—some of them are elements; their common property is that of forming, in combination with hydrogen and with metals, salts. For analytical purposes, then, we may separate the substances

<sup>1</sup> The meaning and use of chemical symbols will be briefly explained hereafter (40.); but the student is presumed to be already acquainted with them. In par. 558 will be found a list of the symbols of the different elements.

we have to detect into the groups of Metals and Acid-radicles. In trying the reactions for these substances it is usual to employ, not the substances themselves, but certain compounds—usually salts—which contain them.

For convenience in hasty writing it is not uncommon to employ abbreviations for the compound radicles, especially for such as are constantly met with or are of unusual complexity. In the text the only such abbreviations employed are:

Am for  $(NH_4)$ , the metallic-radicle ammonium.

T “  $(C_4H_4O_6)$ , the acid-radicle of tartaric acid and the tartrates.

A “  $(C_2H_3O_2)$ , the acid-radicle of acetic acid and the acetates.

Cfy “  $(FeCy_6)$ , the acid-radicle of ferro- and ferri-cyanides.

Ho “  $(HO)$ , the radicle hydroxyl, occurring in hydrates, etc.

**37. Analytical Groups.**—The metals are separated by their behavior with certain general reagents into five principal groups, two of these being further subdivided into two sub-groups. Each of these groups receives a distinctive name,—either a number from its place in the system, or a name from some conspicuous or important member of the group, or from the general reagent used to precipitate the group. Thus we speak indifferently of the 4th Group, the Barium Group, or the Ammonium-carbonate Group. On pages 190 and 191 will be found a table showing the analytical groups with their distinctive numbers, names, and group reagents placed at the head of each column; the names and symbols of the elements contained in the group are arranged vertically beneath.

It is, perhaps, well to avoid referring to a group by its number, as different analysts number the groups differently, and the name thus given is therefore apt not to denote the group with certainty.

**38. Method of Trying the Analytical Reactions in Section IV.**—In order to become fully acquainted with the

behavior of different substances with "reagents," and thus to be able to detect them by their "reactions," each of these reactions should be performed with the substance itself or with one of its compounds, and the appearance presented carefully observed, so that the substance would be easily recognized in a body of unknown composition by means of those tests.

The following general rules must be carefully attended to in trying the reactions; they may be read through before commencing the reactions (par. 47):

1. A *solution* of the substance which is directed to be used must always be employed, unless it is specially stated that the *solid* is required. Solid substances are required as a rule only for blowpipe reactions. A solution can be readily made from the solid, if necessary, by warming it with water, or in some cases with dilute acid (529). This is often called the "original solution."

2. Commence by taking in a test-tube or small beaker a small quantity (about 15–20 cc.) of the solution of the substance. If the solid substance is also required, take some of it upon a watch glass.

3. Pour a small portion of the solution into a perfectly clean test-tube, and add the first-mentioned reagent to it. The reagent must always be added in small quantity at first; more can be employed afterwards if excess is required. The student must from the first acquire the habit of working with small quantities both of solutions and reagents.

For each of the reactions a separate portion of the "original solution" is thus poured into a clean test-tube and the required reagent added to it.

4. Before trying each reaction the student must carefully read through the whole of the description of the results he is to obtain; he must then perform the experiment, literally following out the directions given. He must consider it a necessary condition of after-success that each result is obtained precisely as stated in the text, and must never on any account pass on until he has conscientiously satisfied himself that the statements of the book are true, and that he could at any time repeat the test successfully.

**39. Entry in Note-book.**—Each reaction as soon as it has been satisfactorily tried, should be neatly entered in the note-book in a short form. Since nothing so much aids brevity as the symbolic notation commonly used by chemists, the student should invariably adopt this chemical shorthand in entering results. A full account and explanation of chemical notation may be found in any work on theoretical chemistry, and merely a few hints will therefore be given here which will be of special use for the purpose of briefly entering reactions.

**40. Chemical Notation.**—Each element has its corresponding *symbol*, consisting of one or two letters; thus S stands for sulphur, Cl for chlorine. These symbols also stand for one *atom* of each element; by being written one after another they give the *formula* of a compound substance, showing what elements, and how many atoms of each of these elements, its molecule contains; thus KCl stands for one molecule of potassium chloride, a compound of one atom of potassium and one atom of chlorine;  $\text{PtCl}_4$  stands for one molecule of platinum chloride, which consists of one atom of platinum combined with four atoms of chlorine, the small figure placed *below* a symbol to the right denoting how many atoms of that element are present. A number placed before a formula multiplies each symbol in that formula, thus  $2\text{PtCl}_4$  signifies two molecules of platinum chloride, containing altogether two atoms of platinum and eight atoms of chlorine. If two or more symbols are included in brackets any number placed outside, either *before* or *below* the brackets, multiplies each symbol contained in the brackets; thus both  $\text{Sr}(\text{NO}_3)_2$  and  $\text{Sr}_2(\text{NO}_3)$  stand for  $\text{Sr}_2\text{N}_2\text{O}_6$ , and this may also be written  $\text{Sr}_2\text{NO}_3$ . In paragraph 558 will be found a list of the elements, with their symbols and atomic weights; paragraphs 524, 525, 526, 529, and 530 contain a list of the names and corresponding formulæ of all the most common compound substances mentioned in the course of the book. Symbols and formulæ are always used in the text instead of names, but the student can readily find the correspond-



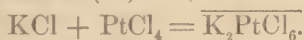
ing names by reference to the above tables, or to the labels on the bottles which should contain both names and formulæ.

41. *Chemical Equations.*—On adding a “reagent” to a substance some change usually occurs which gives rise to an alteration of color, or very frequently to the formation of a precipitate having a certain color, appearance, or behavior with other liquids, which are characteristic of that particular substance, or of some element or group of elements contained in it; this change should be briefly described in the note-book in words, and then represented by a *chemical equation*. The rules for drawing out an equation may be found in any treatise on chemistry; a few general directions only are given here, which will be of service for the special object in question.

42. *Rules for Writing Down an Equation.*—Write down the formulæ of the two substances which are mixed together for the reaction, with the sign of addition (+), between them; then write the sign of equality (=), followed by the formula of the precipitate produced. In a complete equation the formulæ written on the left-hand side of the sign (=) are usually called the “left-hand side” of the equation; those to the right the “right-hand side.” Since most of the following reactions are cases of “double decomposition,”—i. e., cases where a mutual exchange of certain elements or groups of elements occurs between the two compounds,—a little consideration will usually show how many molecules of the substances on the left-hand side of the equation are required to yield the formula for the precipitate, and also whether any other, and if so what other, substance is at the same time formed.

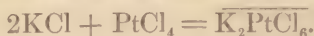
It is always necessary that the number of atoms of any one element on both sides of the equation should be equal. The following are dissected examples:

The first test for K (47):



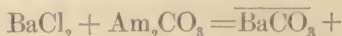
This is simply placing together the substances mixed and the precipitate formed; the equation thus formed is evi-

dently not correct, since we have two atoms of K on the right-hand side and only one on the left, also 6 atoms of Cl on the right and only 5 on the left; but this inequality is at once removed if we place 2 before the KCl, thus:



Evidently if the above equation is correct the precipitate is here the only substance formed, since the number of atoms in the substances on the left-hand side is exactly equal to that in the substance on the right.

Take now the first test for Ba (69):



This represents the substances mixed and the precipitate formed, but evidently the left-hand side of the equation contains more than the right (viz.,  $\text{Am}_2$  and  $\text{Cl}_2$ ); hence we write it fully thus:



which states that on mixing together barium chloride ( $\text{BaCl}_2$ ) and ammonium carbonate ( $\text{Am}_2\text{CO}_3$ ), we obtain barium carbonate ( $\text{BaCO}_3$ ) and ammonium chloride ( $\text{AmCl}$ ).

In writing out these equations a systematic method should be observed. Write down on the left-hand side of the equation first the substance whose reaction is being tried, then the reagent added; and on the right-hand side write first the formula for the precipitate with a line drawn over it by way of distinction, then any substance or substances which may be formed with it.

In the reactions which follow, the formulæ of the substance used, of the reagent added, and of the precipitate produced will always be given, these being sufficient data to enable the student to form the equation; only where the equation is exceptionally difficult or complicated will it be given in full.

43. The following contractions are recommended:

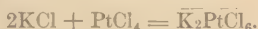
<i>expt.</i>	for	experiment.	<i>insol.</i>	for	insoluble.
<i>pp.</i>	"	precipitate.	<i>soln.</i>	"	solution.
<i>ppn.</i>	"	precipitation.	<i>crystne.</i>	"	crystalline.
<i>ppd.</i>	"	precipitated.	<i>coln.</i>	"	coloration.
<i>sol.</i>	"	soluble.			

44. Examples are given below showing how the reaction should be entered in the note-book; they should be referred to as soon as the student commences the reactions for the metals:

1st. [See pars. 47-50.]

POTASSIUM (K).—Used  $\text{KCl}$ .

$\text{PtCl}_4$ : stirred on watch-glass: yellow cryst<sup>ne</sup> pp., sol. in much water and in  $\text{KHO}$ , insol. in alcohol:



$\text{NaHT}$ : well shaken in a test-tube: white cryst<sup>ne</sup> pp., sol. in water,  $\text{KHO}$ , and  $\text{HCl}$ :



*Flame col<sup>r</sup>*: pale violet, crimson-red through the indigo-prism or cobalt glass.

*Heated in tube or on platinum foil*, solid  $\text{KCl}$  melted, but gave no fumes; hence not volatile.

2d. [See pars. 69-74.]

BARIUM (Ba).—Used  $\text{BaCl}_2$ .

$\text{Am}_2\text{CO}_3$ : white pp., sol. in  $\text{H}\overline{\text{A}}$ :



$\text{CaSO}_4$ : heavy white pp., insol. in boiling  $\text{HCl}$ :



$\text{K}_2\text{CrO}_4$ : light yellow pp., sol. in  $\text{HCl}$ , insol. in  $\text{H}\overline{\text{A}}$ :



*Flame col<sup>r</sup>*: on loop of Pt-wire, yellowish-green color.

45. *General Rules to be Observed whilst Working.*—The student should attend carefully to the following precautions, which will most materially aid the progress and accuracy of his work; if they are observed from the commencement they will not be felt irksome:

1. Before commencing work look through the reagent bottles belonging to the working bench (524); replace any which are absent, and arrange the bottles, if necessary, in the order indicated on an accessible list, or

shown by the number on the labels of the bottles, or by the labels on the edge of the shelf. Then proceed to fill any which are empty and to re-label any whose labels are imperfect or loose. If any of the liquid reagents are not quite clear when shaken they must be filtered before use.

2. Arrange the apparatus required for use, on the hinder part of the bench, so as to leave the front free to work upon; this will lessen the risk of upsetting anything.

3. Before commencing work, all glass and porcelain which is not in use should be carefully cleansed, if not already clean; but it is best never to put apparatus away dirty.

4. In using a reagent bottle take it in the right hand, remove the stopper by taking hold of it between any two of the fingers, or between the fourth finger and palm, of the left hand; hold the stopper in this way and replace it immediately after the bottle has been used. Pour the liquid out at the side opposite to that bearing the label, and prevent the last drop from running down the outside by touching the lip of the bottle either with the stopper or against the clean edge of the vessel. Solid reagents should be taken out of the bottle on a clean knife-blade or spatula, or with a spoon of wood or horn; or a small quantity should be turned out upon a piece of paper or upon the palm of the hand. *The bottle must be re-stoppered and replaced on the shelf in its proper place with the label outwards immediately after use, and must never be left standing on the working bench.*

5. If any solution or precipitate has to be put by for some time, always label it with a piece of gummed paper bearing an inscription or a reference number which is explained in the note-book and is sufficient to recall to mind what the solution or precipitate consists of; never trust to memory in this matter.

6. Brass crucible tongs must never be employed for holding hot evaporating-basins containing acids, as some of the brass is apt to be dissolved and thus introduced

into the solution. A hot dish may be moved either by holding it with a cloth or by lifting the stand upon which the dish is placed.

7. *Liquids only* are to be poured down the sinks; all *solid* refuse, such as soiled filters, broken glass, pieces of charcoal, etc., which would tend to stop the holes in the sink, must be thrown into a box placed in any accessible position in the laboratory, or into a small earthenware jar or vessel placed upon each working-bench.

8. When a student is examining a substance to detect its composition, he must fully write down in his notebook each test or process, with the result obtained, as soon as it is completed. The analysis is thus written out gradually as it progresses; *on no account must the entry of the results be left until the completion of the analysis.* This rule cannot be too strongly enforced, as neglect of it is always attended with loss to the beginner. The most convenient form of entry is that of the analytical tables.

\* \* Cleanliness and neatness in analytical work cannot be too carefully attended to; more confusion and error may be caused by using dirty test-tubes, beakers, dishes, and funnels than would be thought possible by the beginner.

## REACTIONS FOR THE METALS.

*Note.*—In trying through the reactions for the metals, the usual analytical order of the groups has been reversed, because the most simple reactions occur in the last groups, and they are therefore better suited for a beginner.

### GROUP V.—POTASSIUM GROUP.

46. This group includes K,  $\text{NH}_4$ ,<sup>1</sup> Na, Mg. The first three metals (K,  $\text{NH}_4$ , Na) are known as the “alkali metals.”

The members of this group are not precipitated by any of the five group reagents.

<sup>1</sup> A hypothetical metal-radicle, “Ammonium.”



### POTASSIUM (K).—Use KCl.

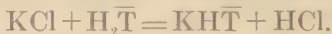
Refer if necessary to paragraphs 38 and 41 for directions how to work.

47.  $PtCl_4$  added after a drop of dilute  $HCl$  to some of the  $KCl$  solution on a watch-glass and stirred with a glass rod, gives a yellow crystalline precipitate ( $K_2PtCl_6$ ), forming first along the lines where the rod has rubbed the glass.

Stir up the precipitate and pour off the liquid with the precipitate into three test-tubes; to one add much distilled water and heat, the precipitate dissolves; to another part add alcohol, the precipitate does not dissolve. Hence this precipitate is soluble in water, insoluble in alcohol. By warming the third portion with solution of  $KHO$ , the precipitate is also shown to be soluble in that liquid.

*Remarks.*—The following remarks are of great importance in using the above test for K. Since this precipitate is soluble in alkalies the liquid should always be neutral or only faintly acid before adding  $PtCl_4$ ; and since it is more insoluble in alcohol than in water, addition of alcohol causes the precipitate to form more rapidly in dilute solutions; owing to the solubility of the precipitate in water, very dilute solutions must however be evaporated nearly to dryness before applying the test. It is always well to add several drops of  $HCl$  before the  $PtCl_4$ , and to make sure by test-paper that the liquid is acid in reaction. These remarks apply also to the precipitate produced by  $PtCl_4$  with ammonium salts (52).

48.  $H_2T$  (or better  $NaHT$ ) mixed with some of the solution in a test-tube gives a white crystalline precipitate ( $KHT$ ); usually this precipitate appears only when the mouth of the test-tube is closed with the thumb, and the tube is well shaken for some time.



Shake up and pour some of the liquid and precipitate into four test-tubes; add to these portions, water,<sup>1</sup>  $KHO$ ,

<sup>1</sup> By "water" is always meant "distilled water," unless otherwise stated.

and  $\text{HCl}$  respectively; on being shaken and warmed the precipitate will dissolve in each of these liquids. Hence this precipitate is soluble in  $\text{H}_2\text{O}$ ,  $\text{KHO}$ , and  $\text{HCl}$ . To the fourth portion add alcohol; the precipitate does not dissolve, since it is insoluble in alcohol.

*Remarks.*—In using the above test for the detection of  $\text{K}$ , the precipitate is not obtained at once in dilute solutions, but its formation is much hastened by the addition of alcohol; very dilute solutions must first be concentrated by evaporation. The solution to be tested should be neutral or only feebly alkaline; if acid in reaction, the acid should be neutralized by  $\text{Na}_2\text{CO}_3$  or boiled off if volatile; feebly acid solutions may, however, be at once mixed with  $\text{NaHT}$ ; to an alkaline solution  $\text{H}_2\text{T}$  should be added till the reaction is strongly acid.

*Note.*—In the following reactions when a precipitate is stated to be soluble or insoluble in certain liquids, it must be proved to be so in the manner described in (47, 48), unless different directions are given.

49. *Flame Coloration* (32).—Hold a loop of platinum wire in the flame and see that it gives no color to the flame; then dip it into some  $\text{KCl}$  solution, or, better still, moisten it and dip it into some powdered  $\text{KCl}$ , and again hold the loop in the upper part of the flame. A *pale-violet* color will be imparted to the flame if the  $\text{KCl}$  is pure;<sup>1</sup> but whatever color is thus seen, the flame-color will always appear *pale blue* or *violet* through the thinner portions of an indigo-prism, and deep *crimson-red* through the thickest parts.

The light of a Bunsen flame itself usually appears pale blue through the indigo-prism; this color should be noted before using the prism for examining a flame coloration.

The flame coloration due to potassium shows in the spectroscope a red line ( $\alpha$ ) and an indigo-blue line ( $\beta$ ) (557).

*Note.*—A piece of blue cobalt glass may be used instead of the indigo-prism, but is by no means to be recommended, as the color of different specimens is somewhat variable in shade and in intensity, whereas the color of the indigo can be obtained of an invariable tint, by dissolving indigo-carmin in water.

50. Heat a little solid  $\text{KCl}$  in a small dry test-tube, or better on a piece of platinum foil; the  $\text{KCl}$  will melt

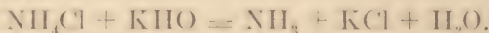
<sup>1</sup>  $\text{KNO}_3$  usually gives a purer potassium coloration.

but will not pass into vapor and produce white fumes unless heated very strongly, since K-salts are non-volatile at a moderate heat. The fused residue is often transparent and invisible if in small quantity; its presence is shown by a slight crackling being heard during cooling.

AMMONIUM ( $\text{NH}_4$ , or Am).—Use  $\text{NH}_4\text{Cl}$  (AmCl).

*Note.*—The symbol Am is often written for  $\text{NH}_4$ ; it is very convenient, as it does away with the necessity of using brackets; e. g.,  $\text{Am}_2\text{S} = (\text{NH}_4)_2\text{S}$ .

51.  $\text{KHO}^1$  (or  $\text{NaHO}$ ) poured into some of the solution, or upon the solid, in a test-tube and heated gives off  $\text{NH}_3$  gas:



This gas is known by the following properties:

a. Its pungent smell—that of common smelling salts.

b. By turning moistened red litmus-paper blue. A small piece of red litmus-paper is wetted with distilled water and placed upon a clean glass rod, and is then held in the test-tube, taking great care not to touch with it the liquid or the sides of the tube; the paper becomes blue.

c. A glass rod dipped into strong  $\text{HCl}$  or strong  $\text{HAc}$ , and held over the mouth of the test-tube, produces dense white fumes.

52.  $\text{PtCl}_4$ , when stirred on a watch-glass with some AmCl solution, gives a yellow crystalline precipitate ( $\text{Am}_2\text{PtCl}_6$ ); this precipitate is soluble in water and in  $\text{KHO}$ , but insoluble in alcohol. The remarks at the end of par. 47 apply here also. This precipitate, if boiled with  $\text{KHO}$ , evolves  $\text{NH}_3$  (difference from  $\text{K}_2\text{PtCl}_6$ ).

53.  $\text{H}_2\text{T}$  (or better  $\text{NaHT}$ ), shaken for some time in a test-tube with AmCl solution, gives a white crystalline precipitate ( $\text{AmHT}$ ), soluble in  $\text{H}_2\text{O}$ ,  $\text{KHO}$ , and  $\text{HCl}$ , insoluble in alcohol. The remarks in par. 48 apply here also.

<sup>1</sup> In all cases where  $\text{KHO}$  is to be used  $\text{NaHO}$  may be substituted, and either  $\text{KHO}$  or  $\text{NaHO}$  may be used unless it is specially stated that "pure  $\text{NaHO}$ " is to be employed.

*Note.*—This precipitate is more soluble than the  $KHT$  precipitate, and therefore does not form so readily. Indeed with  $H_2T$  a precipitate rarely forms unless alcohol is added, in which the precipitate is less soluble than in water. With  $NaHT$  a precipitate is obtained on shaking the liquid well for some time unless it is very dilute.

54. *Flame Coloration.*— $AmCl$ , if pure, gives on platinum wire no color to the flame.

55. *Heat a little solid  $AmCl$*  in a small dry test-tube, or on a piece of platinum foil; it will be converted into vapor producing white fumes, which are seen if platinum foil is used by removing the foil for a moment from the flame; hence  $AmCl$  is volatile.

If the experiment is performed in a dry test-tube, a white coating or "sublimate" forms on the upper part of the tube.

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SODIUM ( $Na$ ).—Use  $NaCl$ .

56. *Flame Coloration.*— $NaCl$  gives an *intense yellow* color to the flame; the color is almost invisible or appears pale blue when viewed through the indigo-prism, *and never shows the slightest tinge of red or purple*, even when seen through the thickest parts of the prism. A crystal of red  $K_2Cr_2O_7$  appears colorless if illuminated by this yellow flame. Examined by a small spectroscope, the sodium coloration gives a single yellow line (*a*) (557).

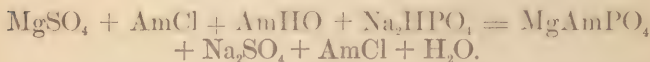
The yellow color of the sodium flame is always readily seen, since it overpowers that of  $K$ ; its production is the most reliable, and often the only possible, test for sodium.

*Note.*—If both  $K$  and  $Na$  are present, the  $K$  coloration is unseen and the yellow coloration of  $Na$  is alone visible; but on examining this flame through the indigo-prism or cobalt glass, the crimson coloration of the  $K$  is at once seen; prove this by mixing together  $KCl$  and  $NaCl$  and trying the flame coloration without and with the indigo-prism. The spectroscope also shows the lines of  $Na$  and  $K$  quite distinct from one another.

57. *Some solid  $NaCl$  heated* in a dry test-tube, or better on platinum foil, melts without producing white fumes unless heated very strongly, since  $NaCl$  is not volatile at a moderate heat.

MAGNESIUM (Mg.).—Use  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  solution.

58.  $\text{Na}_2\text{HPO}_4^1$  added after  $\text{AmCl}$  and  $\text{AmHO}$  gives a white crystalline precipitate ( $\text{MgAmPO}_4$ ); if much water is present this precipitate forms only when the liquid is warmed and well stirred or shaken; it is soluble in acids (use  $\text{HCl}$  or  $\text{HNO}_3$ ), insoluble in  $\text{AmHO}$ .



59.  $\text{KHO}$  gives a white precipitate ( $\text{MgHO}_2$ ),<sup>2</sup> soluble in acids.

60.  $\text{AmHO}$  gives a white precipitate ( $\text{MgHO}_2$ ); but if  $\text{AmCl}$  is added to the  $\text{MgSO}_4$  solution before the  $\text{AmHO}$ , no precipitate is produced.

61.  $\text{Am}_2\text{CO}_3$  gives a white precipitate ( $\text{MgCO}_3$ ), but only in strong solutions and on standing for some time;  $\text{AmCl}$  prevents the formation of this precipitate.

62. *Flame Coloration*.— $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , if pure, gives no color to the flame.

63. *Blowpipe Test*.—A little solid  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  placed in a small cavity on a piece of wood-charcoal and then heated in the tip of the outer blowpipe flame, shines brightly and gives a white unmelted mass of  $\text{MgO}$ ; no white fumes are given off since  $\text{MgO}$  is not volatile. If this white mass after cooling is moistened with several drops of cobalt-nitrate solution and again strongly heated for some time<sup>3</sup> in the outer blowpipe flame, it becomes *delicate pink* in color; this color is best seen when the mass is *quite cold*, by comparison with a white piece of paper held near the residue on the charcoal.

<sup>1</sup>  $\text{NaAmHPO}_4$  is better than  $\text{Na}_2\text{HPO}_4$ , since it produces the precipitate more readily than does  $\text{Na}_2\text{HPO}_4$  in dilute solutions, and always in a crystalline condition.

<sup>2</sup> This convenient symbol ( $\text{HO}$ ) for the group hydroxyl, first proposed by Frankland, will be employed throughout in the formulæ for all hydrates containing more than one atom of hydroxyl; it prevents the necessity of using brackets, as a number placed below the symbol multiplies both  $\text{H}$  and  $\text{O}$ , thus  $\text{HO}_2$  equals  $(\text{HO})_2$  or  $\text{H}_2\text{O}_2$ ; and  $\text{HO}_3$  equals  $(\text{HO})_3$  or  $\text{H}_3\text{O}_3$ .

<sup>3</sup> It is necessary to heat strongly after moistening with  $\text{Co}(\text{NO}_3)_2$ , else blue  $\text{Co}(\text{NO}_3)_2$  remains.



## 64. GROUP V.—TABLE OF DIFFERENCES.

*Note.* A blank thus — signifies that no marked characteristic change occurs. For the method of using the table see par. 65.

Tests.	K—salts.	NH <sub>4</sub> —salts.	Na—salts.	Mg—salts.
1. <i>a. For solutions.</i>				
1. Boil with KHO solution:	—	NH <sub>3</sub> gas given off: known by its smell and by turning moist red litmus blue; it also gives dense white fumes with strong HCl.	—	White precipitate.
2. Heat in flame on clean platinum wire:	<i>Pale violet flame, which appears crimson through the indigo-prism.</i>	—	<i>Intense yellow flame, which shows no tinge of red through the indigo-prism.</i>	—
3. Add AmCl, AmH <sub>2</sub> PO <sub>4</sub> and Na <sub>2</sub> HPO <sub>4</sub> :	—	—	—	White crystalline precipitate.
4. Add PtCl <sub>4</sub> and a drop of dilute HCl and stir vigorously:	Yellow crystalline precipitate, forms only in strong solutions.	Yellow crystalline precipitate, forms only in strong solutions.	—	—
5. Add H <sub>2</sub> T (or better NaHT) and shake well:	White crystalline precipitate in strong solutions.	White crystalline precipitate in strong solutions.	—	—
<i>b. For solids only.</i>				
6. Heat to redness in a dry test-tube, or on platinum foil:	Non-volatile, unless heated to bright redness.	Volatile; white fumes are given off and the substance passes into vapor (at least partially) forming a sublimate on the upper part of the tube.	Non-volatile unless heated to bright redness.	Non-volatile.
7. Heat strongly on charcoal in the outer blow-pipe flame:	Melt easily and sink into the charcoal, coloring the flame pale violet. (See 2.)	Are volatile, giving off white fumes.	Melt easily and sink into the charcoal, coloring the flame intense yellow. (See 2.)	Leave ultimately a white infusible residue which shines brightly, and which if moistened with Co(NO <sub>3</sub> ) <sub>2</sub> solution and re-heated becomes pink.

<sup>1</sup> In using these tests for the detection of a single member of the group in solution, only the first four need be employed; the fifth test may be substituted for the fourth. Tests 6 and 7 are used only for the examination of solids. They may be supplemented, however, by tests 1 and 2.

65. The method of using the foregoing table may be explained in a few words. Suppose a *solution* to be given which is known to contain one member of this group, the first five tests in the table (four and five being alternative) will enable us to decide which member is present. It is simply necessary to examine *separate portions* of the solution by these tests until a result is obtained which conclusively proves the presence of one of the four substances. Tests 1, 2, 6, and 7 are similarly employed for examination of a *solid* substance. The student should never rest content with one test only when a second can be tried in confirmation, and he should always consider the tables of differences as mere summaries, and should refer back to the separate reactions for fuller accounts of the tests when required.

The results of these analyses, and of all analyses subsequently made by using the tables of differences, are best entered in three parallel columns, as shown in the upper part of the table in par. 67. The statement of the experiment or test performed is entered in the first column, the result observed being placed beside it in the second column, whilst beside this in the third column is stated the conclusion inferred from the result obtained.

At the end of each analysis state the result thus: "Found K."

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66. (s)<sup>1</sup> *Detection of Members Mixed.*—We can also devise from the above table a plan for detecting the members of this group when mixed together. It is evident—

1. That  $\text{NH}_4$  can always be detected by boiling with KHO solution.

2. That Na can always be detected by its yellow-flame coloration.

3. That Mg can always be detected by giving a white precipitate on addition of  $\text{AmCl}$ ,  $\text{AmHO}$ , and  $\text{Na}_2\text{HPO}_4$  to its solution.

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<sup>1</sup> Paragraphs marked with an (s) are intended for a student using the senior course, and are passed over in the junior course.

4. That K may always be detected by giving a flame coloration which appears crimson through the indigo-prism.

5. That the confirmatory test for K by stirring with  $\text{PtCl}_4$  may be tried if no  $\text{NH}_4$  is present; but it cannot be employed when  $\text{NH}_4$  has been found, since  $\text{NH}_4$  gives a yellow precipitate exactly like that given by K. Hence  $\text{NH}_4$  is first removed by evaporating some of the solution to dryness, and strongly heating the solid substance thus obtained on platinum foil as long as white fumes come off; the residue (if any) on the foil will then be free from  $\text{NH}_4$ , and can be dissolved and tested for K by  $\text{PtCl}_4$ .

The above remark concerning the  $\text{PtCl}_4$  test applies also to the  $\text{H}_2\text{T}$  test for K, since  $\text{NH}_4$  gives a precipitate with  $\text{H}_2\text{T}$  precisely similar to that yielded by K.

*The following scheme*, which embodies the above tests, must be used to test for Mg, K, Na, and  $\text{NH}_4$ , when they may be present together.

The student should examine several substances by this table for the four members of Group V, writing down the results he obtains fully in the form adopted in the table; that is to say, three columns are ruled; in the first is described the test performed, in the second the result observed, in the third what substance is inferred from that result to be present or absent. After writing out the tests the metals which have been found in the solution are stated thus: "Found K and Na."

\*\*\* Experiment IV in the following table may be omitted by a beginner, K being tested for by the flame coloration alone (EXP. II).

67. (S) TABLE FOR TESTING FOR Mg, K, Na,  $\text{NH}_4$ ,  
IN A SOLUTION WHICH MAY CONTAIN ONE OR ALL  
OF THEM.

(See note at the top of page 101.)

Experiment.	Observation.	Inference.
I. Add to a small part of the solution $\text{AmCl}$ , then $\text{AmHO}$ and $\text{Na}_2\text{HPO}_4$ , shake well and allow to stand if no precipitate appears at once.	1. A white precipitate forms.	Presence of Mg.
	[2. No precipitate appears.]	[Absence of Mg.]
II. Dip a small loop of clean platinum wire into the solution, and hold it near the top of the Bunsen flame.	1. A yellow flame. <sup>1</sup> Look at the yellow flame through the indigo-prism; a crimson-red color is seen.	Presence of Na, possibly also of K.  Presence of K.
	2. A pale-violet flame, appearing crimson red when seen through the indigo-prism.	Presence of K and absence of Na.
	[3. No color is imparted to the flame.]	[Absence of K and Na.]
III. Boil some of the solution in a test-tube with $\text{KHO}$ solution, and try whether $\text{NH}_3$ is given off by smelling; or if it cannot be smelt, by testing with moistened red litmus-paper or strong $\text{HCl}$ .	1. $\text{NH}_3$ gas is smelt, or the red litmus becomes blue, and white fumes are obtained with $\text{HCl}$ .	Presence of $\text{NH}_4$ .
	[2. No $\text{NH}_3$ is smelt, and moist red litmus-paper is not blued, neither are white fumes obtained with $\text{HCl}$ .]	[Absence of $\text{NH}_4$ .]
IV. A confirmatory test for K may be made by adding $\text{PtCl}_4$ or $\text{NaHT}$ . If Exp. III has shown that $\text{NH}_4$ is present, proceed to test for K by column A; if $\text{NH}_4$ is absent, test for K by column B (66, 5).		
A.		B.
Boil some more of the solution down to dryness in a porcelain dish; scrape out the white substance left in the dish, and heat it strongly on a piece of platinum foil as long as any white fumes are seen to be given off when the foil is taken out of the flame for an instant. Place the foil when cold in a test-tube, and boil it with <i>very little</i> water, to which a drop of dilute $\text{HCl}$ has been added, and evaporate to several drops; cool the liquid, and pour it out upon a watch-glass, add a little $\text{PtCl}_4$ , <sup>2</sup> and stir well: A yellow precipitate: <i>Presence of K</i> .		Pour a little of the solution upon a watch-glass, add $\text{PtCl}_4$ , and stir well: a yellow precipitate: <i>Presence of K</i> . If no precipitate forms, K may nevertheless be present, the solution being too dilute to allow the precipitate to form; therefore pour some of the solution into a porcelain dish, boil down nearly to dryness, cool and test this liquid by stirring it with $\text{PtCl}_4$ , <sup>2</sup> on a watch-glass, adding alcohol if the precipitate does not appear at once: a yellow precipitate: <i>Presence of K</i> . <i>Note.</i> —Addition of alcohol will frequently produce the precipitate without evaporation.

<sup>1</sup> Almost all substances contain traces of Na, and therefore when heated in the Bunsen flame tinge it more or less yellow; hence, unless the yellow coloration is very intense, enter in the results "No trace."

<sup>2</sup> In this and all subsequent places where  $\text{PtCl}_4$  is directed to be used as a test for K, the  $\text{NaHT}$  test may be substituted for economical reasons.

*Note.*—Separate portions of the solution are to be used for each of these experiments. It must be understood that *only one* of the numbered results in the second column can be obtained in each experiment, but one or other of these must invariably be observed. In subsequent tables that result only is stated in the second column which indicates the presence of the substance, and the absence of that result proves the absence of the substance; the portions in brackets will therefore be omitted in future.

## GROUP IV.—BARIUM GROUP.

**68.** This group includes Ba, Sr, Ca.

The members of this group differ from those of Group V by being precipitated as carbonates by  $\text{Am}_2\text{CO}_3$ , even in the presence of  $\text{AmCl}$ .<sup>1</sup> They are not precipitated by any other of the group reagents.

**BARIUM (Ba).**—Use  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .<sup>2</sup>

**69.**  $\text{Am}_2\text{CO}_3$  added after some  $\text{AmCl}$ : white precipitate ( $\text{BaCO}_3$ ) which is at first flocculent, but if heated and allowed to stand slowly shrinks in bulk and becomes crystalline.

Pour a little of this into another test-tube and add to it some  $\text{HA}$ , the precipitate dissolves entirely if sufficient  $\text{HA}$  is added.

**70.**  $\text{CaSO}_4$  or  $\text{H}_2\text{SO}_4$ : heavy white precipitate ( $\text{BaSO}_4$ ), insoluble in  $\text{HCl}$  even on boiling.

**71.**  $\text{K}_2\text{CrO}_4$  added after some  $\text{HA}$ : yellow precipitate ( $\text{BaCrO}_4$ ), soluble in warm  $\text{HCl}$ , insoluble in warm  $\text{HA}$ . (Diff. from Sr.)

**72.**  $\text{H}_2\text{SiF}_6$ : semi-transparent precipitate ( $\text{BaSiF}_6$ ): The precipitate often does not appear in dilute solution until after some time, or until the liquid is boiled, or alcohol is added. Shaking or stirring the liquid hastens its formation.

**73.**  $\text{Am}_2\text{C}_2\text{O}_4$ : white precipitate ( $\text{BaC}_2\text{O}_4$ ).

<sup>1</sup> On *boiling* with  $\text{AmCl}$  solution, however, the precipitates are more or less perfectly dissolved.

<sup>2</sup> These two molecules of water are termed "water of crystallization," and are always present in *crystallized* barium chloride.

<sup>3</sup> A reaction in small type is comparatively unimportant, and may be read through and omitted by beginners.



74. *Flame Coloration*:  $\text{BaCl}_2$  gives a yellowish-green color to the flame, visible through the indigo-prism.

The spectrum consists of a number of lines, the most characteristic of which are three green lines,  $\alpha, \beta, \gamma$  (557).

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STRONTIUM (Sr). Use  $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ .

75.  $\text{Am}_2\text{CO}_3$  added after some  $\text{AmCl}$ : white precipitate ( $\text{SrCO}_3$ ), soluble in  $\text{H.A.}$  This precipitate is flocculent at first, but if heated it quickly becomes crystalline and shrinks very considerably.

75 a.  $\text{CaSO}_4$  or  $\text{H}_2\text{SO}_4$ : white precipitate ( $\text{SrSO}_4$ ), this precipitate does not usually form at once in a cold solution, but only after standing for some time. The precipitate, however, *appears at once on boiling the liquid*.

76.  $\text{K}_2\text{CrO}_4$  added after some  $\text{H.A.}$ : no precipitate, since  $\text{SrCrO}_4$  is soluble in  $\text{H.A.}$

77.  $\text{H}_2\text{SiF}_6$ : no precipitate.

78.  $\text{Am}_2\text{C}_2\text{O}_4$ : white precipitate ( $\text{SrCr}_2\text{O}_4$ ).

79. *Flame Coloration*: crimson red; this color appears *intense red* through the indigo-prism unless the flame coloration is very faint.

The strontium spectrum contains many lines; the most characteristic are the orange line ( $\alpha$ ), the red lines ( $\beta, \gamma$ ), and the blue line ( $\delta$ ) (557).

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CALCIUM (Ca).—Use  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ .

80.  $\text{Am}_2\text{CO}_3$  added after  $\text{AmCl}$ : white precipitate ( $\text{CaCO}_3$ ) soluble in  $\text{H.A.}$  This precipitate is flocculent at first, but on standing for some time or on being gently heated it shrinks considerably and becomes crystalline.

81.  $\text{CaSO}_4$ : no precipitate, even on standing or on being boiled.

82.  $\text{H}_2\text{SO}_4$ : white precipitate ( $\text{CaSO}_4$ ) forms at once in strong solutions, and often in weak solutions on being boiled; but since  $\text{CaSO}_4$  is not quite insoluble in water, some of it will always remain dissolved; prove this by boiling the liquid containing the precipitate and filtering

it, then keep adding  $\text{AmHIO}$  to the filtrate and stirring it until a drop of the solution turns red litmus blue and the liquid smells of  $\text{NH}_3$ , then add  $\text{Am}_2\text{C}_2\text{O}_4$ , a white precipitate will form, showing the presence of  $\text{Ca}$  (85), which must have been dissolved as  $\text{CaSO}_4$ .

83.  $\text{K}_2\text{CrO}_4$ : no precipitate.

84.  $\text{H}_2\text{SiF}_6$ : no precipitate.

85.  $\text{Am}_2\text{C}_2\text{O}_4$ : white precipitate ( $\text{CaC}_2\text{O}_4$ ), soluble in most acids except  $\text{HA}$  and  $\text{H}_2\text{C}_2\text{O}_4$ .

86. *Flame Coloration*: yellowish red; this color viewed through the indigo-prism *does not appear red but dingy green*, thus differing from that given by  $\text{Sr}$ .

In the calcium spectrum the most characteristic lines are the green line ( $\beta$ ), and the intense orange line ( $\alpha$ ) (557).

## 87. GROUP IV.—TABLE OF DIFFERENCES.

The first three tests only need be used for the detection of a member of this group occurring by itself in solution; test 1 serves also for solids.

Tests.	Ba—salts.	Sr—salts.	Ca—salts.
1. Flame coloration:	Greenish-yellow.	Intense crimson appears <i>red</i> through the indigo-prism.	Yellowish red, appears <i>dingy green</i> through the indigo-prism.
2. $\text{CaSO}_4$ added to the cold solution:	An immediate precipitate.	A precipitate appearing only after a short time or immediately on boiling.	—
3. $\text{K}_2\text{CrO}_4$ added after $\text{HA}$ :	Light yellow precipitate.	—	—
[4. $\text{H}_2\text{SiF}_6$ added:	White precipitate.	—	— ]
5. $\text{H}_2\text{SO}_4$ added in excess and boiled:	Entirely precipitated as $\text{BaSO}_4$	Entirely precipitated as $\text{SrSO}_4$	Partially precipitated as $\text{CaSO}_4$ ; hence the filtrate from the precipitate contains $\text{Ca}$ , which may be detected by adding $\text{AmHIO}$ in excess, and then $\text{Am}_2\text{C}_2\text{O}_4$ ; a white precipitate forms.

When analyzing a solution which is known to contain only one member of this group, its detection by the first three of the above tests will be exceedingly simple.

88. (s) *The separation and detection of Ba, Sr, and Ca, when mixed*, depends upon the following differences:

1. The flame colorations, examined if necessary through the indigo-prism, or by means of the spectroscope.

2. The difference in behavior with  $\text{CaSO}_4$ , which at once indicates the presence or absence of Ba.

3. The separation of Ba, if present, by  $\text{K}_2\text{CrO}_4$  in the presence of HA.

4. The precipitation of Sr by  $\text{CaSO}_4$  on being boiled, which will indicate the presence of Sr in the absence, or after the separation, of Ba.

5. The precipitation of Sr, if present, by boiling with  $\text{H}_2\text{SO}_4$ ; sufficient  $\text{CaSO}_4$  then remaining in the solution to give, after making the filtrate alkaline with  $\text{AmHO}$ , a precipitate with  $\text{Am}_2\text{C}_2\text{O}_4$ .

89. (s) A solution which has to be examined for Ba, Sr, and Ca, and can contain only these substances, is made alkaline, if not already so, by addition of  $\text{AmHO}$ ; then  $\text{Am}_2\text{CO}_3$  is added as long as it is seen to cause any precipitate after the liquid has been stirred well and allowed to settle. The liquid is then filtered, and a little more  $\text{Am}_2\text{CO}_3$  added to the clear filtrate; if any further precipitate forms, more  $\text{Am}_2\text{CO}_3$  is added and the liquid is again poured through the same filter, pouring the first portion of the filtrate once more through the filter as it is sure to come through turbid. As soon as the filtrate gives no further precipitate with  $\text{Am}_2\text{CO}_3$ , all the members of this group which were present in the solution have been precipitated as carbonates, and on filtration are obtained on the filter. The precipitate is then examined by Table IV (438).

*Note.*—In using the group tables in Section VI, it must be understood that they are drawn out to meet the case of all the members of the group being present. If therefore, in any case no precipitate forms on addition of a reagent, the substance or substances whose presence would have been indicated by the formation of the precipitate must be absent. Hence a filtration which is directed to be made is often unnecessary, and the solution itself is treated as is directed for the filtrate.

## GROUP III A.—IRON GROUP.

90. This group includes Al, Fe, Cr.

The members of this group differ from those of groups III B, IV, and V by being precipitated by AmHO after addition of AmCl; they are not precipitated, however, by the group reagents for Groups II and I.

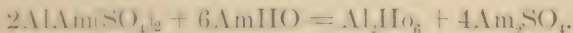
This group is also precipitated by  $\text{Am}_2\text{S}$ , or by  $\text{H}_2\text{S}$  added to the alkaline solution.

Group III A further differs from Group III B in being completely precipitated by adding  $\text{BaCO}_3$  shaken up with water; this reagent affords the most perfect means of separating the two groups.

The members of this group show no characteristic flame colorations; but with the exception of Al, they give borax beads of characteristic color.

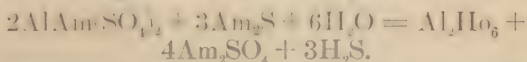
ALUMINIUM (Al).—Use  $\text{AlAm}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  ammonia-alum, or  $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  potash-alum.

91. *AmHO*: white flocculent precipitate ( $\text{Al}_2\text{HO}_6$ ), which is seen best on boiling the liquid; soluble in HCl and in HAc; slightly soluble in AmHO, especially in the absence of AmCl:



92. *KHO* added in very small quantity: same precipitate as AmHO; soluble in excess of KHO. If to a part of the KHO solution HCl be added gradually until it is neutral, the  $\text{Al}_2\text{HO}_6$  is reprecipitated; if more acid is added the precipitate dissolves, but is reprecipitated by adding AmHO in excess. From another portion of the KHO solution the  $\text{Al}_2\text{HO}_6$  may be reprecipitated by addition of sufficient AmCl.

93.  $\text{Am}_2\text{S}$ : same precipitate ( $\text{Al}_2\text{HO}_6$ ),  $\text{H}_2\text{S}$  gas coming off or remaining dissolved in the liquid:



94. *Blowpipe Reaction*.—Some solid  $\text{AlAm}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  heated on charcoal in the outer blowpipe flame,

then moistened, after cooling, with  $\text{Co}(\text{NO}_3)_2$  solution, and again heated in the outer flame, gives a *fine blue mass*.

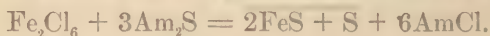
**95. IRON (Fe).**—Two classes of iron compounds are known, which differ in appearance and properties and behave differently with reagents; they are distinguished as *ferrous* and *ferric* compounds respectively, the former being supposed to contain the metal *ferrosum* ( $\text{Fe}''$ ),<sup>1</sup> the latter *ferricum* ( $\text{Fe}'''$ ). It is usual in stating analytical results to mention in which state of combination the iron exists, and therefore some distinctive tests are described below (101). The whole of the reactions of ferrous compounds are not given, because Fe, if present, is always separated and detected in the course of analysis as ferricum, and ferrosum is tested for by special reactions in the original substance. Ferrous are readily converted into ferric compounds by boiling for a short time with a little strong  $\text{HNO}_3$ , or with  $\text{HCl}$  and a crystal of  $\text{KClO}_3$ .

**FERRICUM ( $\text{Fe}'''$ ).**—Use  $\text{Fe}_2\text{Cl}_6$ .

Ferric salts are usually yellow or reddish-yellow; ferrous salts usually pale green, or white if perfectly dry.

**96.  $\text{AmHIO}$  or  $\text{KHIO}$ :** reddish-brown flocculent precipitate ( $\text{Fe}_2\text{Ho}_6$ ); insoluble in  $\text{KHIO}$ , soluble in  $\text{HCl}$ .

**97.  $\text{Am}_2\text{S}$ :** a black precipitate ( $\text{FeS}$ ), mixed with white S: soluble in boiling acids, insoluble in  $\text{KHIO}$ :



In a very dilute solution of Fe a green color is produced at first by  $\text{Am}_2\text{S}$ , and the black precipitate separates only after a time.

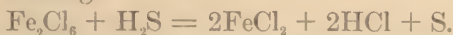
**98.  $\text{H}_2\text{S}$ :**<sup>2</sup> same black precipitate in alkaline solutions: in neutral or acid solutions S is precipitated and the ferric is changed to a ferrous salt, the color of the solution

<sup>1</sup> This distinction of the two conditions of Fe and other elements by dashes or roman numbers placed above the symbol, first proposed by Odling, is very convenient for brevity.

<sup>2</sup>  $\text{H}_2\text{S}$  may be added as a solution of the gas in trying the reactions: in the course of analysis the gas is usually passed into the liquid.



changing from yellow to pale green, as is seen after boiling and filtering:



**99. Blowpipe Reactions.**—These are the same for ferrous as for ferric compounds. Fused with  $\text{Na}_2\text{CO}_3$  on charcoal in the inner flame a gray magnetic powder is left (33 a); this is shown to be magnetic by being attracted when touched under water by the end of a magnet, or of a magnetized knife-blade.

**100. Borax bead:** { Outer flame: *reddish-brown* while hot; *yellow* when cold.  
Inner “ *greenish* bead, the color of green bottle-glass.

### 101. DISTINCTIVE TESTS FOR FERROUS AND FERRIC SALTS.

For these tests several drops of dilute HCl should be first added to the Fe solution.

Reagents to be added.	Ferric salts. (Use $\text{Fe}_2\text{Cl}_6$ solution.)	Ferrous salts. (Use $\text{FeSO}_4$ solution.)
1. $\text{K}_4\text{FeCy}_6$ added in small quantity:	<i>Dark-blue precipitate</i> , “Prussian blue;” insoluble in HCl, <sup>1</sup> soluble in $\text{H}_2\text{C}_2\text{O}_4$ , and slightly soluble in $\text{K}_4\text{FeCy}_6$ added in excess; turned brown by KHO.	<i>Light-blue precipitate</i> , becoming dark blue in the air, or on addition of $\text{HNO}_3$ or Br-water.
2. $\text{K}_6(\text{FeCy}_6)_2$ :	<i>No precipitate</i> : the solution darkens, but on dilution with water is seen to contain no precipitate.	<i>Dark-blue precipitate</i> “Turnbull’s blue;” insoluble in HCl. In <i>very</i> dilute solution only a dark bluish-gray color is produced.
3. $\text{KCyS}$ :	<i>Blood-red coloration</i> : no precipitate is produced, the liquid being perfectly clear on dilution; the color is immediately destroyed when several drops are poured into some $\text{HgCl}_2$ solution; its production is hindered by $\text{HNO}_3$ and by HA.	<i>No red coloration</i> unless small quantities of ferric salts are present.
4. $\text{KHO}$ :	<i>Reddish-brown precipitate</i> .	<i>Dingy-green precipitate</i> , turning brown in the air.

<sup>1</sup> The solubility and insolubility of this precipitate must be shown by warming separate portions of the blue liquid containing the precipitate with HCl,  $\text{H}_2\text{C}_2\text{O}_4$ , and  $\text{K}_4\text{FeCy}_6$ , then separately filtering each; if the precipitate has been dissolved the filtrate will be dark blue.

CHROMIUM (Cr.)—Use  $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , chromalum.

Chromic salts are usually green or violet in color.

102. *AmHIO*: pale bluish-green precipitate ( $\text{Cr}_2\text{H}_6\text{O}_6$ ): if *AmHIO* is added in large quantity and the liquid is heated some of the precipitate is dissolved, producing a beautiful violet-red solution whose color is best seen after filtering; but from this solution the  $\text{Cr}_2\text{H}_6\text{O}_6$  is reprecipitated on boiling the liquid for several minutes in a porcelain dish.

103. *KHIO* added in small quantity gives the same precipitate ( $\text{Cr}_2\text{H}_6\text{O}_6$ ); if more cold *KHIO* is added the precipitate is entirely dissolved to a green fluid; on diluting this liquid with water and boiling for several minutes the  $\text{Cr}_2\text{H}_6\text{O}_6$  is reprecipitated and the liquid becomes colorless. *AmCl* added to the *KHIO* solution also reprecipitates the  $\text{Cr}_2\text{H}_6\text{O}_6$ .

103 a. If to some of the green liquid, obtained by adding *KHIO* in excess to the chromium solution, a little red-lead or lead-peroxide ( $\text{PbO}_2$ ) is added and the liquid is then boiled, a yellow liquid is obtained from which a yellow precipitate ( $\text{PbCrO}_4$ ) is thrown down by addition of *HA* in excess.

104. *AmS* precipitates  $\text{Cr}_2\text{H}_6\text{O}_6$ ,  $\text{H}_2\text{S}$  gas being given off or remaining dissolved. The reaction is similar to that with  $\text{AlAm}(\text{SO}_4)_2$  par. 93.

105. *Blowpipe Reaction*.—If  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  be mixed with any solid substance containing Cr, and the mixture be fused on a piece of platinum foil or in a porcelain crucible or lid, or in a loop of platinum wire as was directed for the borax bead (31), a yellow mass is formed colored by  $\text{Na}_2\text{CrO}_4$ . If this yellow mass is dissolved by boiling it with water, a yellow solution is obtained; this solution, if made acid with *HCl* and boiled for a few minutes to drive off  $\text{CO}_2$ , gives with  $\text{PbA}_2$  solution a yellow precipitate of  $\text{PbCrO}_4$ .

106. Cr forms two classes of compounds: in one class Cr in combination with oxygen functions as an acid-radicle; this class includes the chromates, such as  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ ; they are usually yellow or reddish in color; but Cr also forms a series of salts in which it

acts as a metallic-radicle; these are usually green or violet, and give the above reactions for Cr. The latter compounds pass by oxidation into the former, as in reactions 103 and 105, where the oxidation is caused by  $\text{PbO}_2$  and  $\text{KNO}_3$  respectively. Chromates pass by reduction into the green compounds; examples of this change will be found under the tests for chromic acid 286. This reduction of chromic acid causes it to be detected in the course of analysis as a base, and a special experiment has to be performed to ascertain whether the Cr was present originally as a metallic or as an acid radicle.

## 107. GROUP III A.—TABLE OF DIFFERENCES.

Tests.	Al—salts.	Fe'''—salts.	Fe''—salts.	Cr—salts.
<i>a. For liquids.</i>				
1. Add $\text{AmHO}$ .	White flocculent precipitate.	Reddish - brown flocculent precipitate.	Dismy - green precipitate, rapidly turning brown when left exposed to the air.	Pale-green flocculent precipitate, color unaltered by exposure to air.
2. Add $\text{KHO}$ :	White flocculent precipitate, easily soluble in excess of $\text{KHO}$ .	Reddish - brown flocculent precipitate, insoluble in excess of $\text{KHO}$ .	The same precipitate as with $\text{AmHO}$ , insoluble in excess of $\text{KHO}$ .	Pale-green precipitate, soluble in excess of cold $\text{KHO}$ , but reprecipitated on diluting and boiling for some time.
3. Add $\text{KCys}$ and a few drops of $\text{HCl}$ :	—	Deep blood - red coloration, destroyed by pouring into $\text{HgCl}_2$ solution.	No coloration unless $\text{Fe}'''$ is also present.	—
<i>b. Blow-pipe tests for solids.</i>				
4. Fuse with $\text{Na}_2\text{CO}_3$ and $\text{KNO}_3$ on platinum foil:	—	On cooling a white mass of $\text{Na}_2\text{CO}_3$ remains, with dark - brown particles of $\text{Fe}_2\text{O}_3$ .	Same as $\text{Fe}'''$ .	On cooling a yellow mass remains, easily soluble in water; the solution, after having been boiled with excess of $\text{HA}$ , gives a yellow precipitate with $\text{PbA}_2$ .
5. Heated on charcoal:	In the outer flame when cool if moistened with $\text{Co}(\text{NO}_2)_2$ solution and reheated strongly gives a fine blue mass.	In inner flame mixed with $\text{Na}_2\text{CO}_3$ gives a gray magnetic powder. (33 a.)	Same as $\text{Fe}'''$ .	—
6. Fused in borax bead:	—	Reddish - yellow in outer flame. Greenish-yellow in inner flame.	Same as $\text{Fe}'''$ .	Green both in outer and inner flames.

Members of this group occurring singly are easily distinguished by one or other of the above tests, the first three serving for liquids, the last three for solids; tests 2 and 5 are the best for Al, 2, 4, and 6 for Cr, and 1, 3, or 6 for Fe.

108. (s) *The separation and detection of these three substances when mixed* depend upon the following differences:

1. The solubility of  $\text{Al}_2\text{HO}_6$  in *boiling*  $\text{KHO}$ , in which  $\text{Fe}_2\text{HO}_6$  and  $\text{Cr}_2\text{HO}_6$  are insoluble.

2. The conversion of  $\text{Cr}_2\text{HO}_6$  by fusion with  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  into soluble  $\text{Na}_2\text{CrO}_4$ ;  $\text{Fe}_2\text{HO}_6$  remaining as  $\text{Fe}_2\text{O}_3$ , which is insoluble in water.

3. The yellow color of the solution of  $\text{Na}_2\text{CrO}_4$  in water, and production of a yellow precipitate by acidifying it with  $\text{HA}$  and adding  $\text{PbA}_2$ .

4. The blood-red coloration obtained by adding  $\text{KCys}$  to the  $\text{Fe}_2\text{O}_3$  dissolved in  $\text{HCl}$ .

109. (s) A solution which may contain Al, Fe, Cr, is examined in the following manner:

To a few drops of the solution acidified with  $\text{HCl}$  add a little  $\text{K}_4\text{FeCy}_6$ ; if a blue precipitate is produced Fe is present; this portion is rejected. Two other small portions of the acidified solution are then tested; one with  $\text{K}_6(\text{FeCy}_6)_2$ , which by giving a dark-blue precipitate shows the presence of  $\text{Fe}''$ ; the other with  $\text{KCys}$ , which if it gives a blood-red color proves the presence of  $\text{Fe}'''$ .

Boil the rest of the solution for several minutes, adding a few drops of strong  $\text{HNO}_3$  if  $\text{Fe}''$  is present; add some  $\text{AmCl}$ , then  $\text{AmHO}$  until the liquid after being well stirred is alkaline and smells of  $\text{NH}_3$ ; boil, filter, and examine the precipitate by Table III A (436), disregarding all the appended notes.

## GROUP III B.—ZINC GROUP.

110. This group includes Zn, Mn, Ni, Co; its members differ from those of Groups IV and V, by being precipitated by  $\text{Am}_2\text{S}$  in neutral or alkaline solution, and by  $\text{H}_2\text{S}$  in alkaline solution; they are not precipitated by

the group reagents for Groups III A, II, and I. Mn is, however, liable to be precipitated by AmHIO, even in the presence of AmCl, if the solution stands exposed to air for some time.

The members of this group show no characteristic flame colorations, but with the exception of Zn give characteristic colors to a borax bead.

BaCO<sub>3</sub> does not precipitate this group as it does Group III A, unless its members are present as sulphates.

### ZINC (Zn).—Use ZnSO<sub>4</sub>·7H<sub>2</sub>O.

Zinc salts are usually colorless.

111. Am<sub>2</sub>S: white precipitate (ZnS): the precipitate often appears yellow from the presence of excess of yellow Am<sub>2</sub>S in the liquid; its true color is seen in the next reaction, or by letting the precipitate produced by Am<sub>2</sub>S settle, or by filtering it. For the solubility of this precipitate see the end of the next reaction.

112. H<sub>2</sub>S:<sup>1</sup> white precipitate (ZnS): the Zn is only partly precipitated from a neutral solution, since H<sub>2</sub>SO<sub>4</sub> is separated and dissolves the ZnS:



but if NaHIO or AmHIO be added to neutralize the H<sub>2</sub>SO<sub>4</sub> when it is set free, the Zn may be entirely precipitated; addition of NaA also causes complete precipitation, since HA replaces H<sub>2</sub>SO<sub>4</sub> in the solution, and ZnS is insoluble in HA:



Add H<sub>2</sub>S to some ZnSO<sub>4</sub> solution to which AmCl has been first added and then AmHIO until it is alkaline, and show by adding to separate portions of this liquid HCl, H $\bar{\text{A}}$ , and Am<sub>2</sub>S, that ZnS is soluble in HCl, and insoluble in H $\bar{\text{A}}$  and in Am<sub>2</sub>S.<sup>2</sup>

<sup>1</sup> H<sub>2</sub>S may be used in this group as sulphuretted hydrogen water.

<sup>2</sup> The tests which show the solubility of the sulphides of this group are best tried on the precipitate obtained by adding AmCl, AmHIO,



**113.**  $KHO$  added in small quantity gives a white precipitate ( $ZnHO_2$ ); if more  $KHO$  is added, this precipitate dissolves; the  $ZnHO_2$  is, however, reprecipitated as such by adding much water to this solution and boiling it, or as  $ZnS$  by passing  $H_2S$  gas into it.

**114.** Solid  $ZnSO_4 \cdot 7H_2O$  powdered with  $Na_2CO_3$  in a mortar, then heated on charcoal in the inner blowpipe flame, gives an incrustation on the charcoal, which is *yellow* whilst hot and white when cold. It cannot be driven away by the outer blowpipe flame, but is easily removed by the inner flame. If this incrustation on cooling is moistened with cobalt-nitrate solution and strongly heated in the outer blowpipe flame it becomes *green*.

The above changes of color are more distinctly obtained by igniting a little solid  $ZnSO_4$  in the outer blowpipe flame on charcoal; it is *yellow* whilst hot, and *white* when cold; if moistened with  $Co(NO_3)_2$  solution and reheated in the outer flame, it becomes *green*.

### MANGANESE (Mn).—Use $MnCl_2$ or $MnSO_4$ .

Manganous salts are usually of a pale-pink color. Alkaline manganates are green, permanganates purple.

**115.**  $Am_2S$ : flesh-colored or pale-pink precipitate ( $MnS$ ): the liquid should be filtered, since the precipitate often appears discolored by the yellow  $Am_2S$ , the color of the precipitate on the filter is then easily seen; the color of the moist precipitate changes to dark brown on standing in the air upon the filter. For the solubility of this precipitate see (116).

**116.**  $H_2S$  precipitates  $MnS$  partly from neutral solutions, entirely from alkaline solutions, but not at all in presence of free  $HCl$  or  $HAc$ ; show with separate portions of the  $MnS$  precipitate, obtained by adding  $AmCl$ ,  $AmHO$ , and then  $H_2S$  solution to the liquid, that  $MnS$  is soluble in  $HCl$  and in  $HAc$ , but insoluble in  $Am_2S$ .

**117.**  $KHO$ : white precipitate ( $MnHO_2$ ), quickly turned brown by pouring the liquid containing the pre-

and  $H_2S$ , unless freshly prepared colorless  $Am_2S$  can be obtained, since from yellow  $Am_2S$  acids precipitate sulphur.

precipitate into a white porcelain dish or upon a filter: the precipitate is insoluble in excess of  $\text{KHO}$ .

**118.**  $\text{AmHIO}$  gives the same precipitate, but if sufficient  $\text{AmCl}$  is first added,  $\text{AmHIO}$  produces no immediate precipitate; the solution, however, on standing exposed to the air turns brown and the  $\text{Mn}$  is gradually precipitated as brown  $\text{Mn}_2\text{HO}_6$ .

**118 a.** Pour a little  $\text{MnSO}_4$  (not  $\text{MnCl}_2$ ) solution upon some red or brown lead oxide ( $\text{PbO}_2$ ), add  $\text{HNO}_3$ , which must be quite free from  $\text{Cl}$ ; boil the mixture and allow the powder to settle; the clear liquid is colored deep red by the formation of permanganic acid ( $\text{HMnO}_4$ ). The production of this color is prevented by the presence of even a minute quantity of chlorine.

**119. Blowpipe Tests.**—If any solid substance containing  $\text{Mn}$  be fused in the outer flame with a mixture of  $\text{Na}_2\text{CO}_3$  and a little  $\text{KNO}_3$  upon platinum foil, a *bluish-green mass* is obtained on cooling; the mixture should be fused by heating the lower surface of the foil with the blowpipe flame. The test may be also made by fusing a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  into a bead in a loop of platinum wire, and then fusing the substance into this bead by heating it in the extreme tip of the outer flame.

**119 a.** Fused with  $\text{Na}_2\text{CO}_3$  on charcoal in the inner flame, a gray magnetic powder is obtained (33 a).

**120. Borax Bead.**—Use *very* little  $\text{MnO}_2$ :<sup>1</sup>  
 In the outer flame { *Violet-red* bead whilst hot.  
                               *Amethyst-red* on cooling.  
 In the inner flame.—A colorless bead.

**NICKEL (Ni).**—Use  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ .

Nickel salts are usually bright green in color.

**121.**  $\text{Am}_2\text{S}$ : black precipitate ( $\text{NiS}$ ); add more *yellow*  $\text{Am}_2\text{S}$ ,<sup>2</sup> boil and filter, a brown filtrate runs through,

<sup>1</sup> A borax bead is often opaque from the use of too much substance. If such is the case fuse the bead in the blowpipe flame, then by a sudden jerk throw some of the fused mass off, and fuse again the remaining portion with fresh borax; repeat this if necessary. The fused bead often becomes transparent when flattened by squeezing with small pincers.

<sup>2</sup> The  $\text{Am}_2\text{S}$  must be yellow; colorless  $\text{Am}_2\text{S}$  does not dissolve  $\text{NiS}$ .

colored by  $\text{NiS}$  dissolved in the excess of  $\text{AmS}$ ; pour this filtrate into a porcelain dish and boil for some time, adding distilled water if necessary to prevent the dish becoming dry; the black  $\text{NiS}$  will be precipitated and may be filtered off, giving a colorless filtrate. If  $\text{HAc}$  is added to the dark filtrate until it is acid, the  $\text{NiS}$  is also precipitated from it.

**122.**  $\text{H}_2\text{S}$ : black precipitate ( $\text{NiS}$ ) in neutral solutions or in solutions acid with  $\text{HAc}$  (112), but  $\text{HCl}$  prevents the precipitation; show with portions of the liquid containing  $\text{NiS}$ , obtained by adding  $\text{H}_2\text{S}$  to  $\text{NiSO}_4$  solution to which a little  $\text{AmCl}$  and  $\text{AmHIO}$  have been added, that  $\text{NiS}$  is insoluble in cold dilute  $\text{HCl}$  and in  $\text{HAc}$ , but soluble when heated with  $\text{HCl}$  after adding a crystal of  $\text{KClO}_3$ .

**123.**  $\text{KHIO}$ : light-green precipitate ( $\text{NiHIO}_2$ ).

**124.**  $\text{AmHIO}$  added in very small quantity: bluish-green precipitate ( $\text{NiHIO}_2$ ), soluble in excess of  $\text{AmHIO}$  to a violet-blue liquid, soluble also in  $\text{AmCl}$ . If  $\text{AmCl}$  be first added,  $\text{AmHIO}$  causes no precipitate.

**125.**  $\text{KCy}$  solution<sup>1</sup> added in small quantity gives a yellowish-green precipitate ( $\text{NiCy}_2$ ); by further addition of  $\text{KCy}$  this precipitate is dissolved, but  $\text{HCl}$  reprecipitates  $\text{NiCy}_2$  from the solution.

**126.** If some  $\text{NiSO}_4$  solution is made acid with several drops of  $\text{HCl}$ , then  $\text{KCy}$  solution gradually added, whilst stirring or shaking the liquid, until the precipitate is redissolved, and the solution thus obtained is boiled for a short time, then cooled and divided into two parts:  $\text{HCl}$  added in excess to one part will produce a precipitate of  $\text{NiCy}_2$ , often only appearing after a time:  $\text{Na}_2\text{Cl}_2\text{O}$ , or  $\text{Br}$ -water after excess of  $\text{NaHIO}$ , added to the other part will give on warming a black precipitate ( $\text{Ni}_2\text{HIO}_6$ ).

#### *Blowpipe Reactions:*

**127.** Solid  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  powdered with  $\text{Na}_2\text{CO}_3$  in a mortar and then fused on charcoal in the inner blowpipe flame, leaves a gray powder which is attracted by the magnet. (33 a).

<sup>1</sup>  $\text{KCy}$  solution must always be prepared immediately before use; it is decomposed by keeping.

**128. Borax bead :**

In outer flame	{	<i>Violet or sherry-red bead whilst hot.</i>
		<i>Pale yellow on cooling.</i>
In inner flame, after being heated for some time.	}	<i>Black or opaque bead.</i>

**COBALT (Co).—Use  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .**

Cobalt salts are usually reddish-pink in color.

**130.  $\text{Am}_2\text{S}$ :** black precipitate ( $\text{CoS}$ ) ; on adding much  $\text{Am}_2\text{S}$ , boiling and filtering, the filtrate is colored yellow by  $\text{Am}_2\text{S}$  and is not dark colored, since  $\text{CoS}$  is insoluble in  $\text{Am}_2\text{S}$  (difference from  $\text{NiS}$ ). For the solubility of  $\text{CoS}$  see Exp 131.

**131.  $\text{H}_2\text{S}$ :** black precipitate ( $\text{CoS}$ ), only forms in alkaline solutions or in solutions acid with  $\text{HAc}$  (112);  $\text{HCl}$  prevents the precipitation. Add  $\text{AmCl}$ , then  $\text{AmHIO}$  in excess, and then  $\text{H}_2\text{S}$ -water to some  $\text{Co}(\text{NO}_3)_2$  solution, and pour into separate portions of this liquid  $\text{HCl}$  and  $\text{HAc}$ , the precipitate does not dissolve; to the portion containing  $\text{HCl}$  add a crystal of  $\text{KClO}_3$  and heat, the precipitate dissolves readily.

**132.  $\text{KHIO}$ :** blue precipitate ( $\text{CoHIO}_2$ ), turning green if poured out upon a watch-glass and allowed to stand in the air, and becoming pale red on being boiled; the red color is, however, frequently more or less masked by a brown cobalt hydrate precipitated at the same time.

**133.  $\text{AmHIO}$ :** bluish-green precipitate, having the same properties as that given by  $\text{KHIO}$ ; soluble in  $\text{AmCl}$ , hence if  $\text{AmCl}$  is added before  $\text{AmHIO}$  no precipitate is produced.

**134.  $\text{KCy}$**  solution added in small quantity gives a reddish-brown precipitate ( $\text{CoCy}_2$ ); add more  $\text{KCy}$  solution slowly and whilst shaking the liquid, the precipitate dissolves; now add  $\text{HCl}$ , the  $\text{CoCy}_2$  is reprecipitated.

**135.** If some  $\text{Co}(\text{NO}_3)_2$  solution is made acid with a few drops of  $\text{HAc}$ , then  $\text{KCy}$  solution added slowly until the precipitate at first formed just redissolves, and the

liquid is boiled until no further smell of  $\text{HCy}$  is evolved, then cooled and divided into three parts, it will be found that neither  $\text{HCl}$ , nor  $\text{Na}_2\text{Cl}_2\text{O}$ , nor Br-water with excess of  $\text{NaHO}$  solution, produces a precipitate on warming the liquid. [Difference from  $\text{Ni}$  (126).]

The difference of behavior of the  $\text{Ni}$  and  $\text{Co}$  solutions which have been boiled with excess of  $\text{KCy}$ , is due to the fact that  $\text{NiCy}_2$  forms with  $\text{KCy}$  a feeble compound ( $\text{NiCy}_2 \cdot 2\text{KCy}$ ), which is soluble in water, but is easily decomposed; whereas  $\text{CoCy}_2$  forms with  $\text{KCy}$  in the air the very stable soluble compound  $\text{K}_6(\text{CoCy}_6)_2$  "Potassium cobalticyanide."

### Blowpipe Reactions:

**136.** Fused with  $\text{Na}_2\text{CO}_3$  on charcoal in the inner flame  $\text{Co}(\text{NO}_3)_2$  gives a gray metallic powder attracted by the magnet (33 a).

### 139. GROUP III

Tests.	Zn—salts.	Mn—salts.
<i>a. For liquids.</i>		
1. Add $\text{Am}_2\text{S}_3$ or better, $\text{AmCl}$ , $\text{AmHO}$ in excess, and $\text{H}_2\text{S}$ -water:	White precipitate: soluble in cold dilute $\text{HCl}$ : insoluble in $\text{HAc}$ .	Pink precipitate: soluble in cold dilute $\text{HCl}$ : soluble in $\text{HAc}$ .
2. Add $\text{KHO}$ :	White precipitate: soluble in excess of $\text{KHO}$ .	White precipitate: turning brown in the air: insoluble in $\text{KHO}$ .
3. Add $\text{KCy}$ , solution: This test need only be tried when a black precipitate has been obtained by Test No. 1.	—	—
<i>b. Blowpipe tests for solids.</i>		
4. Fused with $\text{Na}_2\text{CO}_3$ :	On charcoal in the inner flame: gives a white incrustation, which, if moistened with $\text{Co}(\text{NO}_3)_2$ and heated in the outer flame, turns green. The substance itself when strongly heated after having been moistened with $\text{Co}(\text{NO}_3)_2$ also becomes green.	On charcoal in the inner flame: a gray magnetic powder (33 a). On platinum foil in outer flame: a bluish-green mass showing more rapidly if a little $\text{KNO}_3$ be mixed with the $\text{Na}_2\text{CO}_3$ before fusing.
5. Borax bead:	—	Outer flame.—Amethyst-red. Inner flame.—Colorless.



**137.** *Boric bead*: strong solution may be employed, the bead being dipped into it; *fine blue* bead in both inner and outer flames; opaque if too much  $\text{Co}(\text{NO}_3)_2$  has been used.

**138.** When a solution is to be examined for only one member of this group, its detection by one or more tests in the table (139) will be very easy. The precipitate with  $\text{Am}_2\text{S}$  is distinctive,  $\text{ZnS}$  and  $\text{MnS}$  being equally recognized by their different colors;  $\text{NiS}$  and  $\text{CoS}$ , which differ from  $\text{ZnS}$  and  $\text{MnS}$  by being black, are distinguished from one another by the solubility of  $\text{NiS}$  in excess of  $\text{Am}_2\text{S}$ , the liquid therefore giving a brown filtrate.  $\text{KHO}$  also gives characteristic precipitates with

TABLE OF DIFFERENCES.

Ni—salts.	Co—salts.
<i>Black precipitate: soluble in boiling yellow <math>\text{Am}_2\text{S}^1</math> to a dark solution: insoluble in cold dilute <math>\text{HCl}</math> and in <math>\text{HAc}</math>.</i>	<i>Black precipitate: insoluble in boiling yellow <math>\text{Am}_2\text{S}^1</math> in cold dilute <math>\text{HCl}</math>, and in <math>\text{HAc}</math>.</i>
<i>Green precipitate: insoluble in <math>\text{KHO}</math>.</i>	<i>Blue precipitate: insoluble in <math>\text{KHO}</math>.</i>
Added in excess to the slightly acid solution and boiled for some time, then $\text{Na}_2\text{CO}_3$ (or $\text{Br}$ -water and excess of $\text{NaHO}$ ) added, gives a black precipitate on heating.	Added in excess to slightly acid solution and boiled for some time, $\text{Na}_2\text{CO}_3$ (or $\text{Br}$ -water and excess of $\text{NaHO}$ ) gives no precipitate on heating.
On charcoal in the inner flame, a gray magnetic powder (33 a).	Same as Ni.
Outer flame. $\left\{ \begin{array}{l} \text{Violet or yellow while hot.} \\ \text{Yellow when cold.} \end{array} \right.$ Inner flame.— <i>Gray or opaque</i> bead.	Outer and inner flames.— <i>Fine blue</i> bead.

order to ascertain whether the precipitate has been dissolved, filter and observe if the filtrate is dark in color.

each of these substances. The most distinctive tests for Ni and Co are 3 and 5; for Zn and Mn, 2, 4, and 5.

**140.** (s). *The method for separating and detecting Zn, Mn, Ni, Co, when mixed, depends on:*

1. The solubility of NiS in yellow  $\text{Am}_2\text{S}$ ; ZnS, MnS and CoS being insoluble.<sup>1</sup> NiS is precipitated from this solution by boiling or by addition of HAc, and the presence of Ni is then confirmed by fusion in a borax bead.

2. The solubility of ZnS and MnS in cold dilute HCl, NiS and CoS being almost insoluble. (Note 1, below.)

3. The solubility of  $\text{ZnH}_2\text{O}_2$  in cold  $\text{KHO}$ , in which  $\text{MnH}_2\text{O}_2$  is insoluble; white ZnS is then precipitated from this solution by  $\text{H}_2\text{S}$ .

4. The production of a bluish-green mass by fusing  $\text{MnH}_2\text{O}_2$  with  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$ .

5. The difference of behavior of the KCy solution of Ni and Co with  $\text{Na}_2\text{Cl}_2\text{O}$ , or with Br-water and excess of NaHO; and the marked difference in their borax beads. (Note 2, below.)

*Note 1.*—Mn may also be separated from Ni and Co by passing  $\text{H}_2\text{S}$  into the solution containing  $\text{NaA}$  (112); Mn remains in solution, NiS and CoS are precipitated.

*Note 2.*—A modification by Henry of Rose's method for separating Ni and Co is also to be recommended; it depends upon the fact that, whilst Co is precipitated as  $\text{Co}_2\text{H}_2\text{O}_6$  by  $\text{BaCO}_3$  in presence of Br, Ni remains in solution. The sulphides are dried and then strongly ignited in an open porcelain crucible; the metals remaining as oxides are dissolved by boiling with a little strong HCl, carbon is filtered off if necessary, and to the clear solution, after being cooled and mixed with Br-water, excess of  $\text{BaCO}_3$  is added in a small corked flask; the flask is then well shaken and allowed to stand for about half an hour; on filtering, Co if present is detected in the precipitate by the borax bead; Ni is precipitated from the filtrate by heating it with KHO; on filtering, the presence of Ni in the precipitate may be confirmed by fusing a portion of it in the borax bead.

**141.** (s). A solution is examined for Zn, Mn, Co, Ni, by adding AmCl to it in a boiling-tube, then  $\text{AmHO}$  if necessary until it is alkaline, and then  $\text{Am}_2\text{S}$  until, after being well stirred or shaken, the liquid smells of it. The liquid is then boiled, a few drops are poured upon a fil-

<sup>1</sup> In order to ascertain whether the precipitate has been dissolved, filter and observe whether the filtrate is dark in color.

ter and the color of the filtrate noted; if it is colorless, sufficient  $\text{Am}_2\text{S}$  has not been added; more  $\text{Am}_2\text{S}$  is then to be poured in, and the liquid again boiled. When a few drops run through the filter brown or yellow in color,  $\text{Am}_2\text{S}$  has been added in excess; the whole is boiled and filtered and the precipitate examined by Table III B (437); the filtrate if yellow is rejected, if brown it is examined for Ni according to (431).

## GROUP II A.—COPPER GROUP.

142. This group includes  $\text{Hg}''$ , Pb, Bi, Cu, Cd; its members differ from those of Groups III A, III B, IV and V, in being precipitated by  $\text{H}_2\text{S}$  in acid solutions. With the exception of Pb, which in a strong solution is partially precipitated by  $\text{HCl}$ , the members of this group are not precipitated by  $\text{HCl}$ .

The sulphides differ from those of Group II B, by being insoluble in  $\text{Am}_2\text{S}$  or  $\text{KHO}$ . If very much acid is present,  $\text{H}_2\text{S}$  does not precipitate the members of this group readily or completely; they are precipitated however on dilution.

### MERCURICUM ( $\text{Hg}''$ ).—Use $\text{HgCl}_2$ .

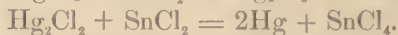
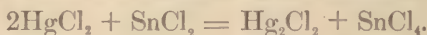
143.  $\text{Hg}$  forms two series of compounds distinguished as *mercuric* and *mercurous*; the mercury in these two states behaves differently with reagents, and may be distinctively called *mercuricum* and *mercurosum*; in the latter state it is classed under Group I.

144.  $\text{H}_2\text{S}$ :<sup>1</sup> black precipitate ( $\text{Hg}_2\text{S}$ ): if the  $\text{H}_2\text{S}$  solution is added slowly, the precipitate is first *white*, then *brown* or *orange*, and ultimately becomes *black*: these changes of color during the addition of  $\text{H}_2\text{S}$  are characteristic of mercuric salts. Filter and wash the precipitate: place portions of it in three test-tubes: boil one portion with strong  $\text{HNO}_3$  and another with strong  $\text{HCl}$ , the precipitate is not dissolved by either acid; mix the contents of the two tubes and warm again, the precipi-

<sup>1</sup> A test-tube half full of the solution must be used in order to get sufficient precipitate for the experiments below. This remark applies also to the liquid used for obtaining the  $\text{H}_2\text{S}$ -precipitate with the other members of this group.

tate will now dissolve: boil the third portion with  $\text{Am}_2\text{S}$ , the precipitate does not dissolve. Hence  $\text{HgS}$  is insoluble in hot strong  $\text{HNO}_3$ , in hot strong  $\text{HCl}$ , and in  $\text{Am}_2\text{S}$ , but is easily soluble in a mixture of  $\text{HNO}_3$  and  $\text{HCl}$  or "aqua regia."

145.  $\text{SnCl}_2$ : white precipitate ( $\text{Hg}_2\text{Cl}_2$ ): if more  $\text{SnCl}_2$  is added and the liquid boiled, the white precipitate becomes gray and consists of fine particles of  $\text{Hg}$ ; if the liquid be decanted and the gray precipitate be then boiled with strong  $\text{HCl}$ , the  $\text{Hg}$  particles unite to globules visible by a lens or frequently by the naked eye.



146. *Cu*: if a small strip of copper sheet or a copper coin, whose surface has been polished and cleansed by rubbing it with sandpaper, be immersed in some  $\text{HgCl}_2$  solution made acid with a drop or two of  $\text{HCl}$ , it will soon become coated with a gray film of  $\text{Hg}$ :



If the surface of the *Cu*, after having been immersed for several minutes, is dried and rubbed hard with a cloth or piece of wash-leather, it will appear more or less whitened like silver, the liquid metal  $\text{Hg}$  having "amalgamated" the *Cu*. The  $\text{Hg}$  may be readily driven off by heating the *Cu* strongly; if this heating is performed in a test-tube, or better in a small hard glass tube sealed at one end (10), a sublimate of globules of  $\text{Hg}$  forms upon the cool sides of the tube.

147. Mix a *little* solid  $\text{HgCl}_2$  intimately with about three times as much  $\text{Na}_2\text{CO}_3$ , by powdering them together in a mortar, or with a pestle on a watch-glass. Pour some of this dried mixture into a perfectly dry small test-tube (see note below), and cover the mixture with a small layer of  $\text{Na}_2\text{CO}_3$ ; now heat strongly first the layer of  $\text{Na}_2\text{CO}_3$ , then gradually the mixture:  $\text{Hg}$  will sublime, condensing in globules on the sides of the tubes. Sometimes the globules are so small that the layer appears as a gray film; they may be united into

visible globules by rubbing the film with a splinter of wood or with a thin glass rod (11 *a*), or the separate globules may be seen by means of a pocket lens.

*Note.*—The powdered mixture is best dried by spreading it out upon a watch-glass and placing it in a stream or water oven; it may be dried also by supporting it on the filter-dryer (25) at some height above a *small* flame. A powder such as the above is most easily placed in a narrow closed tube by alternately scooping the powder up with the mouth of the tube, and tapping the tube so as to shake the power to the bottom, or by turning the powder out upon a piece of note-paper folded over into a trough and pouring it thence into the tube, holding both over the watch-glass to catch any substance which falls. Both the inside of the tube and the powder must be perfectly dry, else some powder obstinately adheres to the sides of the tube and obscures the sublimate. The heating must never be commenced until the sides of the tube are perfectly clean; they are cleansed if necessary with a twisted slip of filter-paper or a wooden match; also if any drops of water condense on the inside of the tube during the first stage of the heating they must be removed by a twisted piece of filter-paper, or by a small piece of filter-paper rolled round a wooden match or a thin piece of wire.

148. Heat a little solid  $\text{HgCl}_2$  in a tube closed at one end; the substance sublimes in white fumes, since Hg-compounds are volatile.

LEAD (Pb).—Use  $\text{Pb}\bar{\text{A}}_2 \cdot 3\text{H}_2\text{O}$  dissolved in water to which a little HA has been added.

149.  $\text{H}_2\text{S}$ : black precipitate ( $\text{PbS}$ ): this precipitate is red if much hydrochloric acid is present in the solution, but becomes black on diluting with water and passing  $\text{H}_2\text{S}$ , or on adding more  $\text{H}_2\text{S}$ -solution. Filter or decant, and show with separate portions of the precipitate that  $\text{PbS}$  is insoluble in  $\text{KHO}$  or  $\text{Am}_2\text{S}$ , soluble in boiling dilute  $\text{HNO}_3$ , but converted by boiling strong  $\text{HNO}_3$  into insoluble  $\text{PbSO}_4$ .

150.  $\text{HCl}$ : white precipitate ( $\text{PbCl}_2$ ), forms only in cold and strong solutions: on boiling, the precipitate dissolves,<sup>1</sup> but the  $\text{PbCl}_2$  separates again in beautiful crystals on cooling.

151.  $\text{H}_2\text{SO}_4$ : white precipitate ( $\text{PbSO}_4$ ): this precipitate is much less soluble in dilute  $\text{H}_2\text{SO}_4$  than in water,

<sup>1</sup> If the precipitate does not entirely dissolve add a little water and boil again.



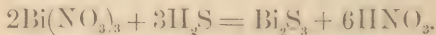
hence  $\text{H}_2\text{SO}_4$  should be added in excess to a pretty strong solution of Pb: pour off into two test-tubes and let the liquid stand; decant the liquid from the precipitate, and show that the precipitate may be dissolved by pouring upon it  $\text{HAc}$  or  $\text{H}_2\text{T}$ , then  $\text{AmHO}$  in excess, and boiling; show also that it dissolves in boiling strong  $\text{HCl}$ .

152.  $\text{K}_2\text{CrO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ : yellow precipitate ( $\text{PbCrO}_4$ ); pour off into two tubes and show that the precipitate is soluble in  $\text{KHO}$ , but insoluble in  $\text{HAc}$ .

153. *Blowpipe Reaction*.—Mix well some powdered  $\text{PbA}_2 \cdot 3\text{H}_2\text{O}$  with about twice as much  $\text{Na}_2\text{CO}_3$ ; heat the mixture in a cavity on a piece of charcoal in the inner flame; a yellow incrustation will form around the cavity and small bright white-globules of Pb will be seen within it. The incrustation is readily removed when heated in the inner blowpipe flame, coloring the flame azure-blue. Detach one of the globules with the point of a knife, place it on the bottom of a mortar turned upside down, and give it a smart blow with the pestle; it flattens out without breaking into powder, because Pb is *malleable*, not *brittle*. If one of the globules be fixed upon the point of a penknife, it will be found by gentle friction on paper to mark it as a black-lead pencil does.

BISMUTH (Bi).—Use  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  dissolved in dilute  $\text{HCl}$ .

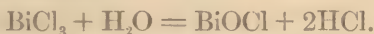
154.  $\text{H}_2\text{S}$ : brownish-black precipitate ( $\text{Bi}_2\text{S}_3$ ): let stand and decant most of the water; then pour some of the precipitate into three test-tubes, and show that it is insoluble in  $\text{Am}_2\text{S}$ , and in  $\text{KHO}$ , but soluble in strong  $\text{HNO}_3$ .



155.  $\text{AmHO}$  or  $\text{KHO}$ : white precipitate ( $\text{BiHO}_3$ ): pour off a small quantity of the liquid and precipitate into a tube, add much  $\text{AmHO}$  and warm, the precipitate is undissolved; filter off the rest of the precipitate and dissolve it by pouring upon the filter a few drops of hot dilute  $\text{HCl}$ ; keep this solution.

156.  $\text{H}_2\text{O}$ : pour the  $\text{HCl}$  solution obtained from the

last reaction, or some of the original solution, into a large quantity of distilled water contained in a beaker; on stirring and letting stand a milkiness appears, due to the formation of  $\text{BiOCl}$ .



Pour a little of the milky liquid into two test-tubes; warm one portion after adding to it a little strong  $\text{HCl}$ , the precipitate dissolves; to the other add  $\text{H}_2\text{T}$  and warm, the milkiness remains (difference from  $\text{SbOCl}$ ). If but little  $\text{Bi}$  is present this milkiness often only appears after stirring and letting the liquid stand for five or ten minutes.

157.  $\text{K}_2\text{CrO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  (see note below): yellow flocculent precipitate  $[\text{Bi}_2(\text{CrO}_4)_3]$ : add  $\text{KHO}$ , the precipitate does not dissolve (difference from  $\text{PbCrO}_4$ ); it dissolves completely in  $\text{HCl}$  or  $\text{HNO}_3$  added in excess.

*Note.*—Since this precipitate is soluble in  $\text{HCl}$ , and  $\text{HCl}$  is present in the  $\text{Bi}$ -solution used, the free  $\text{HCl}$  must first be removed by dissolving in a little of the  $\text{Bi}$ -solution a sufficient quantity of solid  $\text{NaA}$ ; the free  $\text{HCl}$  is thus replaced by  $\text{HA}$ , which does not dissolve the precipitate:



158.  $\text{H}_2\text{SO}_4$ : no precipitate.

159. *Blowpipe Reaction.*—A mixture of powdered  $\text{Bi}(\text{NO}_3)_3$  and  $\text{Na}_2\text{CO}_3$ , heated on charcoal in the inner flame, gives an incrustation *orange-red* whilst hot, *yellow* when cold; also white globules of  $\text{Bi}$ , which are very brittle, being crushed to powder by a sharp blow with a pestle (153).

**COPPER (Cu).**—Use  $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ .

Copper salts are usually blue, sometimes green in color; their color commonly becomes very pale, or disappears when the salts are thoroughly freed from water of crystallization.

160.  $\text{H}_2\text{S}$ : brownish-black precipitate ( $\text{CuS}$ ): filter, keeping the funnel carefully covered with a glass plate, as air quickly oxidizes  $\text{CuS}$  to  $\text{CuSO}_4$ , which dissolves and runs through with the filtrate. Place some of the precipitate in five test-tubes, and show that it is insoluble in  $\text{KHO}$ , in  $\text{Am}_2\text{S}$ , and in boiling dilute  $\text{H}_2\text{SO}_4$ , but dis-

solves in boiling  $\text{HNO}_3$ , dilute or strong, and in  $\text{KCy}$  solution.

**161.**  $\text{AmHIO}$  added in very small quantity: a *greenish-blue* precipitate: if more  $\text{AmHIO}$  is added this precipitate dissolves, yielding an *intensely blue* liquid containing  $(\text{N}_2\text{CuAm}_4\text{H}_2)\text{SO}_4$ , which becomes again light blue on adding an acid in excess.

**162.**  $\text{H}_2\text{SO}_4$ : no precipitate.

**163.**  $\text{K}_4\text{FeCy}_6$ : reddish-brown precipitate ( $\text{Cu}''_2\text{FeCy}_6$ ), insoluble in  $\text{HAc}$ ; the color is best seen by trying the reaction in a white porcelain dish. In *very* dilute solution only a reddish color is produced.

**164.**  $\text{Fe}$ : a bright strip of steel or iron, such as the blade of a penknife, freed from grease by rubbing with sandpaper, or by boiling in a dilute  $\text{KHO}$  and washing, when dipped into  $\text{CuSO}_4$  solution made acid with a few drops of  $\text{H}_2\text{SO}_4$ , is covered with a red film of  $\text{Cu}$  after a time.

**165.**  $\text{Zn}$  and  $\text{Pt}$ :  $\text{Zn}$  if placed upon a piece of platinum foil or wire in some  $\text{CuSO}_4$  solution contained in a porcelain dish or watch-glass, causes a red film of  $\text{Cu}$  to deposit on the platinum. The  $\text{CuSO}_4$  solution should be first made acid with a few drops of  $\text{H}_2\text{SO}_4$ .

#### *Blowpipe Reactions:*

**166.** A mixture of powdered  $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$ , if heated on charcoal in the inner blowpipe flame, gives red scales of  $\text{Cu}$ , which are best seen by separating them as directed in (33 a).

**167.** *Borax bead.*

{	In outer flame:	{	Green whilst hot, blue when cold.
	In inner flame:		Red or colorless bead when cold; obtained only when very little $\text{Cu}$ is present, and the bead is long heated in a good reducing flame. <sup>1</sup>

<sup>1</sup> The red bead is much more easily and rapidly obtained by fusing a fragment of  $\text{Sn}$  or  $\text{Zn}$  into the bead; the former gives a clear, the latter a turbid bead.

**168.** *Flame coloration*: a loop of platinum wire dipped into  $\text{CuSO}_4$  solution, and held in the inner blowpipe flame, or in the Bunsen flame, gives a *green* coloration; the flame shows a *blue centre* after the loop has been moistened  $\text{HCl}$ .

CADMIUM ( $\text{Cd}$ ).—Use  $\text{CdSO}_4 \cdot 4\text{H}_2\text{O}$ .

**169.**  $\text{H}_2\text{S}$ : bright-yellow precipitate ( $\text{CdS}$ ): boil off the  $\text{H}_2\text{S}$ , and pour the liquid into several tubes; show with these separate portions that the precipitate is insoluble in  $\text{Am}_2\text{S}_3$ , in  $\text{KHIO}$ , and in  $\text{KC}_y$  solution, but soluble in boiling dilute  $\text{HNO}_3$  and in boiling dilute  $\text{H}_2\text{SO}_4$ ; dilute the  $\text{H}_2\text{SO}_4$  solution with much water and pass  $\text{H}_2\text{S}$  for a short time, yellow  $\text{CdS}$  is reprecipitated.

**170.**  $\text{AmHIO}$  added in small quantity, best by using  $\text{AmHO}$  much diluted: white precipitate ( $\text{CdHIO}_2$ ); on adding more  $\text{AmHIO}$  the precipitate readily dissolves.

**171.**  $\text{H}_2\text{SO}_4$ : no precipitate.

**172.** *Blowpipe Reaction*.—Powdered  $\text{CdSO}_4$  mixed with  $\text{Na}_2\text{CO}_3$  and heated on charcoal in the inner blowpipe flame, gives a brown incrustation.

**173.** GROUP II A.—TABLE OF DIFFERENCES.—(See pp. 126, 127.)

**174.** The color of the  $\text{H}_2\text{S}$  precipitate, and its behavior with strong  $\text{HNO}_3$ , enable the analyst to detect one member of this group when present alone: the most characteristic special tests for each member of this group will be found under its reactions.

**175.** (s). The separation of  $\text{Hg}$ ,  $\text{Pb}$ ,  $\text{Bi}$ ,  $\text{Cu}$ ,  $\text{Cd}$ , depends upon the following differences:

1. The solubility of  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$  in strong boiling  $\text{HNO}_3$ ;  $\text{HgS}$  and  $\text{PbS}$  being insoluble, and remaining as  $\text{HgS}$  and  $\text{PbSO}_4$ .

2. The solubility of  $\text{PbSO}_4$  in  $\text{H}\bar{\text{A}}$  and excess of  $\text{AmHO}$ ;  $\text{HgS}$  being insoluble.

3. The solubility of  $\text{CuHIO}_2$  and  $\text{CdHIO}_2$ , and insolubility of  $\text{BiHIO}_3$ , in excess of  $\text{AmHO}$ .

4. The solubility of  $\text{CdS}$  and insolubility of  $\text{CuS}$  in boiling dilute  $\text{H}_2\text{SO}_4$ . The insolubility of  $\text{CdS}$  in  $\text{KC}_y$

solution, in which  $\text{CuS}$  easily dissolves, furnishes another means of separation.

After having been separated, the presence of each metal is confirmed by some special test.

**176.** (s). *A solution which may contain Pb, Hg, Bi, Cu, Cd, mixed, is first made acid, if not already so, with a little  $\text{HCl}$ ;  $\text{H}_2\text{S}$  is then passed in a rapid stream through the solution for about five minutes; the precipitate is filtered off, the filtrate mixed with  $\text{H}_2\text{S}$  water, or diluted with a little water and  $\text{H}_2\text{S}$  again passed for a short time,*

## GROUP II A.

Tests.	Hg—salts.	Pb—salts.
<i>a. For liquids.</i>		
1. Pass $\text{H}_2\text{S}$ , or add $\text{H}_2\text{S}$ water:	Black precipitate; when filtered and well washed, insoluble in boiling strong $\text{HNO}_3$ , and unchanged by it.	Black precipitate; almost insoluble in boiling strong $\text{HNO}_3$ , changed by it into white $\text{PbSO}_4$ .
2. Add $\text{H}_2\text{SO}_4$ :	—	White precipitate.
3. Add $\text{AmHO}$ :	White precipitate, insoluble in excess.	White precipitate, insoluble in excess.
<i>b. Blowpipe reactions for solids.</i>		
4. Heated with $\text{Na}_2\text{CO}_3$ on charcoal in the inner blowpipe flame:	Test for Hg by (147).	Yellow incrustation; white malleable globules.

<sup>1</sup> A white precipitate of  $\text{PbCl}_2$ , which may form if the solution is very strong, is neglected, since it is readily convertible into  $\text{PbS}$  by  $\text{H}_2\text{S}$ .



to ascertain whether all the metals have been completely precipitated: if no further precipitate is produced the filtrate may be rejected; but in case  $\text{H}_2\text{S}$  causes further precipitation, the gas must be passed for some time longer, and the liquid poured again through the filter, the filtrate only being rejected when  $\text{H}_2\text{S}$  no longer produces any precipitate in it; the precipitate is then examined by Table II (435), commencing at Group II A (Copper Group), and using only the left-hand side of the table.

TABLE OF DIFFERENCES.

Bi—salts.	Cu—salts.	Cd—salts.
<i>Black</i> precipitate; soluble in boiling strong $\text{HNO}_3$ to form a colorless solution.	<i>Black</i> precipitate; soluble in boiling concentrated $\text{HNO}_3$ to form a blue solution; insoluble in boiling dilute $\text{H}_2\text{SO}_4$ .	<i>Yellow</i> precipitate; soluble in boiling $\text{HNO}_3$ , and in boiling dilute $\text{H}_2\text{SO}_4$ .
White precipitate, insoluble in excess.	Blue precipitate, easily soluble in excess to a deep-blue liquid.	White precipitate, easily soluble in excess.
Confirm by (156).		
<i>Orange-red</i> incrustation; white <i>brittle</i> globules.	No incrustation; red metallic scales. Confirm by (167, 168).	<i>Brown</i> incrustation; no globules.

## GROUP II B.—ARSENIC GROUP.

177. This group includes As, Sb, Sn; its members differ from those of Groups III A, III B., IV, and V, by being precipitated by  $\text{H}_2\text{S}$  in a solution made acid with  $\text{HCl}$ ; they differ from those of Group I, in not being precipitated by  $\text{HCl}$ .

The sulphides of this group, which are precipitated by  $\text{H}_2\text{S}$ , differ from those of Group II A by being soluble in  $\text{Am}_2\text{S}$  or  $\text{KHO}$ .

178. Each member of this group forms two series of compounds which resemble each other in many reactions, but also present several differences. The two classes are distinguished conveniently by the terminations *-ic* and *-ous*, thus we speak of arsenic and arsenious acid.

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ARSENIC (As).	{	For arsenious compound use $\text{HCl}$ solution of $\text{As}_2\text{O}_3$ . For arsenic compound use water so- lution of $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ .
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A. TESTS WHICH GIVE ULTIMATELY THE SAME RESULT WITH BOTH SETS OF COMPOUNDS.

The two solutions should be taken in separate test-tubes and a portion of each tried in succession with each reagent; the difference of behavior is thus more easily appreciated and remembered.

Arsenic compounds are converted into arsenious by boiling with  $\text{HCl}$ ; this explains reactions (179) and (180) with arsenic solutions.

Reagent.	Arsenious solution.	Arsenic solution.
179. $\text{H}_2\text{S}$ :	In neutral solutions only a yellow color is produced, but if the solution is acid with $\text{HCl}$ a light yellow flocculent precipitate ( $\text{As}_2\text{S}_3$ ) forms immediately even in the cold. Shake up and pour some of the liquid into another test-tube and show that $\text{KHO}$ and $\text{Am}_2\text{S}$ , added to the separate portions drop by drop dissolve the precipitate, which, however, is thrown down again on addition of $\text{HCl}$ in excess. <sup>1</sup>	No precipitate is produced in the cold solution acidified with $\text{HCl}$ ; but if the acid solution is boiled, $\text{H}_2\text{S}$ causes in the hot solution, first a milky precipitate of $\text{S}$ , then yellow $\text{As}_2\text{S}_3$ .
180. $\text{Cu}$ : 3 or 4 narrow strips brightly polished with sand-paper.	<i>Reinsch's test.</i> —If boiled in the solution to which some dilute $\text{HCl}$ has been added, $\text{Cu}$ becomes coated with a black film ( $\text{As}_2\text{Cu}_3$ ); if the $\text{Cu}$ strips are carefully dried by being pressed between filter-paper, and are heated in a small dry test-tube, a white sublimate of $\text{As}_2\text{O}_3$ forms in the upper part of the tube; on being examined with a lens, this is seen to consist of white octahedral crystals. This sublimate may be dissolved when cold in a little hot water, and the presence of $\text{As}$ confirmed by tests (179) and (187). The presence of $\text{As}$ in the deposit should always be confirmed in this way, since other metals besides $\text{As}$ are deposited on $\text{Cu}$ as a black film.	The same deposit is obtained as with $\text{As}_2\text{O}_3$ , but only when strong $\text{HCl}$ is added and the liquid boiled.

<sup>1</sup> The  $\text{KHO}$  solution of the precipitate and the  $\text{As}_2\text{S}_3$  precipitated from it by  $\text{HCl}$  are often discolored by black sulphides formed by the action of  $\text{H}_2\text{S}$  upon  $\text{Pb}$  or  $\text{Fe}$  present as an impurity in the  $\text{KHO}$ ; this discoloration may be almost entirely prevented by boiling the liquid before adding  $\text{KHO}$ ,—the free  $\text{H}_2\text{S}$  is thus expelled.

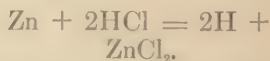
TESTS DEPENDING ON THE FORMATION OF  $\text{AsH}_3$ .

*Note 1.*—As  $\text{AsH}_3$  is a very poisonous gas, the following experiments should be performed in a cupboard provided with a good draught, or in the open air.

*Note 2.*—Arsenic compounds give these reactions less readily than arsenious, but by being boiled with  $\text{HCl}$  for a short time they are converted into arsenious compounds, which then readily give the following reactions.

**181. Hofmann's Method.**—If some scraps of  $\text{Zn}$  and some dilute  $\text{HCl}$ , both free from  $\text{As}$ , be placed together in a small flask fitted with a funnel-tube dipping below

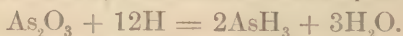
the liquid and a delivery-tube, as shown in Fig. 33,<sup>1</sup>  $\text{H}$  will be given off either at once or on adding a little strong  $\text{HCl}$ :



The hydrogen can be made to bubble through some  $\text{PbA}_2$  solution contained in a second small flask connected with the

first by a piece of india-rubber tubing; the gas, thus freed from any  $\text{H}_2\text{S}$  with which it might possibly have been mixed, is then allowed to bubble through some  $\text{AgNO}_3$  solution contained in a test-tube which is supported in a small beaker; if the  $\text{Zn}$  and acid were free from  $\text{As}$ , no precipitate or color is produced in the  $\text{AgNO}_3$  solution.

If a little  $\text{As}_2\text{O}_3$  solution be now poured into the larger flask through the funnel, a black precipitate ( $\text{Ag}$ ) will begin to form in the  $\text{AgNO}_3$  solution; this is produced by the  $\text{AsH}_3$  evolved by the action of the  $\text{H}$  upon the  $\text{As}_2\text{O}_3$ :



<sup>1</sup> In order to be sure that the corks and tubes fit air-tight, moisten the outside of the cork after it has been placed in the neck of the flask and, having closed one tube, blow down the other. No air-bubbles must be seen or heard to escape. Several of these apparatus may be kept ready fitted in the laboratory for general use.

FIG. 33.



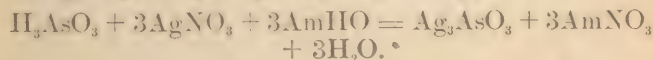
The  $\text{AsH}_3$  on passing into the  $\text{AgNO}_3$  solution, reacts thus:



Hence Ag is precipitated, and  $\text{H}_3\text{AsO}_3$  remains in solution.

As soon as a copious precipitate has been obtained, the test-tube is removed. It will be best to put by the test-tube with its contents to be examined afterwards as directed below, and whilst the gas is coming off to proceed at once to use it for reactions (182) and (183).

The liquid in the test-tube is filtered, the precipitate rejected, and several drops of  $\text{AgNO}_3$  solution are added to the clear filtrate. On mixing with this liquid drop by drop some very dilute  $\text{AmHO}$ ,<sup>1</sup> and stirring or shaking after each addition, a light-yellow precipitate ( $\text{Ag}_3\text{AsO}_3$  or  $\text{Ag}_2\text{HAsO}_3$ ) will be obtained. The formation of this precipitate on addition of  $\text{AmHO}$ , is explained by the fact that  $\text{H}_3\text{AsO}_3$  is in the solution in the presence of  $\text{AgNO}_3$  and also of  $\text{HNO}_3$  (see last equation); now  $\text{AgNO}_3$  forms with  $\text{H}_3\text{AsO}_3$  a yellow precipitate ( $\text{Ag}_3\text{AsO}_3$ ) if no free acid is present in the liquid (187); hence on neutralizing with  $\text{AmHO}$  the free  $\text{HNO}_3$  already present, and that which is formed by the action of  $\text{AgNO}_3$  on  $\text{H}_3\text{AsO}_3$ , the precipitate appears:



This precipitate is also readily soluble in  $\text{AmHO}$ ; hence great caution is requisite to use very dilute  $\text{AmHO}$ , and to add it gradually.

*Caution.*—Both flasks should be rinsed out each time after use, else some of the  $\text{AsH}_3$  may remain in them and be driven out in a future operation.

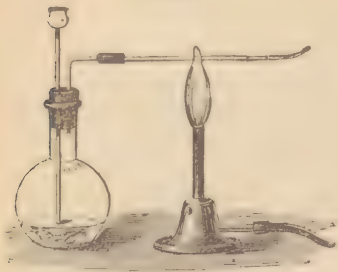
**182.** Disconnect the larger flask from the smaller, and slip into the india-rubber joint a tube of hard glass about four inches in length whose end is drawn out to a fine jet, and supported on the ring of the retort-stand

<sup>1</sup> Made by pouring several drops of  $\text{AmHO}$  solution into a test-tube, then nearly filling up with distilled water and shaking the tube.



(Fig. 34); if the gas is not coming off briskly pour in through the funnel-tube a little strong  $\text{HCl}$  and light the gas as it issues from the jet.<sup>1</sup> The flame will differ from

FIG. 34.



that of pure  $\text{H}$  by burning with a bluish tinge, and by giving off white fumes of  $\text{As}_2\text{O}_3$ .<sup>2</sup>

Press down upon the flame the inside of a porcelain crucible lid or of a porcelain crucible or dish,—a dusky black film of  $\text{As}$  will be deposited upon the cool surface; pour upon this some  $\text{Na}_2\text{Cl}_2\text{O}$

solution,—the stain is rapidly dissolved. Warm also a stain of  $\text{As}$ , obtained inside a porcelain dish, with  $\text{Am}_2\text{S}_3$ ; it will dissolve and on gentle evaporation will leave *yellow*  $\text{As}_2\text{S}_3$ .

183. Add a little more strong  $\text{HCl}$  if necessary to cause the gas to come off rapidly, light it at the jet and heat a point near the middle of the tube strongly (see Fig. 34); a black mirror of  $\text{As}$  will form just beyond the part heated by the flame, and the flame burning at the jet will meanwhile become colorless, showing that the arsenic has been removed from the hydrogen. Heat another point in the tube so as to produce a second mirror; then divide the tube between the mirrors, and show by warming one portion when cold with

FIG. 35.



<sup>1</sup> If the experiment is performed as here directed, the  $\text{H}$  will have been evolved for some time before being lighted, and there is no fear of an explosion occurring; but if the  $\text{H}$  is being produced for the first time, allow it to escape briskly for four or five minutes, and ascertain that a test-tube full of the gas burns quietly (see Exp. 8, p. 26) before adding the liquid to be tested for  $\text{As}$  and lighting the gas at the jet.

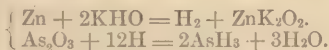
<sup>2</sup> If these appearances are not noticeable, pour a little more  $\text{As}_2\text{O}_3$  solution into the flask through the funnel and mix by gentle shaking.

some  $\text{Na}_2\text{Cl}_2\text{O}$  solution in a test-tube, that the mirror is soluble in  $\text{Na}_2\text{Cl}_2\text{O}$ ; show that the other, when heated in the tube held obliquely in the flame, or bent as shown in Fig. 35 gives a sublimate of  $\text{As}_2\text{O}_3$ . Dissolve the sublimate when cool in a little hot water and confirm the presence of As by reactions (179) and (187).

Tests (182) and (183) were first suggested by *Marsh*; the former is usually known as *Marsh's test*.

**183 a.**  $\text{AsH}_3$  produces a characteristic color with  $\text{HgCl}_2$  solution. Remove the cork from the larger flask and push a plug of cotton-wool into its neck to stop any spirting from the liquid in the flask, then cover the mouth of the flask with a small piece of filter-paper moistened with  $\text{HgCl}_2$  solution. The paper becomes colored first *yellow* then *brown*.

**184.** If some pieces of Zn or Al be boiled in  $\text{KHO}$  solutions II is evolved, which is free from odor, but if a little  $\text{As}_2\text{O}_3$  solution be now added and the liquid be again boiled, a garlic odor is evolved owing to the formation of  $\text{AsH}_3$ :



If a small slip of filter-paper moistened with  $\text{AgNO}_3$  solution and placed on the end of a glass rod,<sup>1</sup> be held in the gas in the mouth of the tube whilst the liquid is being boiled, the paper will be stained black by the separation of Ag (181).

This reaction does not succeed with arsenic compounds unless they are first reduced by boiling with  $\text{HCl}$ . It is not given by any Sb compounds (difference between As and Sb).

**185.** If any solid substance containing As be mixed with powdered  $\text{Na}_2\text{CO}_3$  and  $\text{KCy}$  or with  $\text{K}_2\text{C}_2\text{O}_4$  in a

FIG. 36.



mortar, and a small quantity of the mixture, after having been dried for some time at a gentle heat on a watch-glass,

<sup>1</sup> A simple method of getting a moistened piece of paper on the rod is to dip the rod into  $\text{AgNO}_3$  solution; then gently press the paper slip upon it whilst the rod is wet.

be introduced into a little bulb-tube of hard glass (Fig. 36) or small test-tube at least three inches in length; and if the substance be then heated, observing the precautions stated in the note under (147), a black mirror of As forms in the cooler part of the tube and frequently a smell of garlic may be detected at the mouth of the tube. If the tube be cut off and the mirror be heated by holding the bulb obliquely in the flame (Fig. 35), or if the As be resublimed in the test-tube, the mirror is converted into a sublimate of  $\text{As}_2\text{O}_3$  crystals.

**186. Blowpipe Reaction.**—If any solid substance containing As is mixed with  $\text{Na}_2\text{CO}_3$  and the mixture is heated on charcoal in the inner blowpipe flame, a smell of garlic is produced, which is noticed if the charcoal is removed from the flame and smelt. The flame is also colored *livid blue*.

A little solid  $\text{As}_2\text{O}_3$  heated in a small ignition-tube is readily “sublimed,” and the sublimate is seen under a microscope or a powerful lens to consist of octahedral crystals.

## B. DISTINCTIVE TESTS FOR ARSENIOUS AND ARSENIC COMPOUNDS.

Reagent.	Arsenious compound. Use $\text{As}_2\text{O}_3$ dissolved in $\text{HCl}$ except for (187).	Arsenic compound. Use $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ dissolved in $\text{H}_2\text{O}$ .
<b>187.</b> $\text{AgNO}_3$ , several drops are added to a solution of $\text{As}_2\text{O}_3$ in water. For this reaction $\text{As}_2\text{O}_3$ dissolved in boiling water is employed, because $\text{HCl}$ would yield a precipitate of $\text{AgCl}$ .	<i>Light-yellow precipitate</i> ( $\text{Ag}_2\text{HAsO}_3$ or $\text{Ag}_3\text{AsO}_3$ ): this precipitate forms only on adding carefully, drop by drop, a little dilute $\text{AmHO}$ : <sup>1</sup> show that it is dissolved by $\text{AmHO}$ and by $\text{HNO}_3$ . It is also appreciably soluble in $\text{AmNO}_3$ : hence, if too much $\text{AmHO}$ has been added, the precipitate does not always form on neu- tralizing with $\text{HNO}_3$ .	<i>Brown precipitate</i> ( $\text{Ag}_3\text{AsO}_4$ ): show that it is soluble in $\text{AmHO}$ and in $\text{HNO}_3$ .
<b>188.</b> $\text{CuSO}_4$ , several drops:	<i>Yellowish-green precipitate</i> ( $\text{Cu}'\text{HAsO}_3$ ): this precip- itate forms only on adding dilute $\text{AmHO}$ carefully, drop by drop: <sup>2</sup> show that it is soluble in $\text{AmHO}$ and in $\text{HNO}_3$ .	<i>Pale-green precipitate</i> ( $\text{CuHAsO}_4$ ): soluble in $\text{AmHO}$ and in $\text{HNO}_3$ .
<b>189.</b> $\text{CuSO}_4$ , two drops: then $\text{KHO}$ added:	The above yellowish-green precipitate is first pro- duced, but on addition of more $\text{KHO}$ this dissolves to a clear <i>blue</i> liquid, which on being boiled deposits <i>red</i> $\text{Cu}_2\text{O}$ .	No clear blue solution is obtained, and no $\text{Cu}_2\text{O}$ is produced on boiling the liquid.
<b>190.</b> $\text{AmCl}$ , $\text{AmHO}$ , and $\text{MgSO}_4$ :	No precipitate.	White crystalline pre- cipitate ( $\text{MgAmAsO}_4$ ): if filtered off and moistened with $\text{AgNO}_3$ solution on the filter it becomes <i>brown</i> .

<sup>1</sup>  $\text{As}_2\text{O}_3$  when dissolved in water yields  $\text{H}_2\text{AsO}_3$ , which cannot give with  $\text{AgNO}_3$  the  $\text{Ag}_3\text{AsO}_3$  precipitate, because this decomposition would liberate  $\text{HNO}_3$ , in which  $\text{Ag}_3\text{AsO}_3$  is soluble; hence the addition of  $\text{AmHO}$  is necessary to neutralize the free acid; but since the precipitate is also soluble in  $\text{AmHO}$ , the latter must be added carefully in only just sufficient quantity to neutralize the acid. This is best effected by using some very dilute  $\text{AmHO}$ , made by pouring a few drops into a test-tube, filling the tube two-thirds with distilled water, then closing it with the thumb, and inverting it for a moment. The dilute  $\text{AmHO}$  is to be added drop by drop, shaking or stirring the test solution after each addition until the precipitate is obtained.

<sup>2</sup> The precipitate produced by  $\text{CuSO}_4$  is soluble in acids, hence the  $\text{HCl}$  present in the solution must be neutralized by careful addition of  $\text{AmHO}$  before the precipitate will appear.

**ANTIMONY (Sb).**—Use  $\text{SbCl}_3$ , or  $2\text{KSbOT.H}_2\text{O}$  “Tar-tar emetic,” dissolved in dilute  $\text{HCl}$ .

Antimonic compounds give results ultimately identical with antimonious in the following eight reactions, except in (192). After these reactions, which are common to Sb in both its sets of compounds, are given two which are distinctive; they are, however, rarely used and may be neglected by the student.

**191.**  $\text{H}_2\text{S}$ : orange-red precipitate ( $\text{Sb}_2\text{S}_3$ ): pour into two tubes and show that the precipitate is dissolved when warmed with pure  $\text{NaHO}$  or with  $\text{Am.S}$ , but is reprecipitated from these solutions on addition of  $\text{HCl}$  in excess.

**192.** If poured into much water,  $\text{SbCl}_3$  solution yields a white precipitate or turbidity ( $\text{SbOCl}$ ); this precipitate redissolves on adding  $\text{HCl}$  and warming, and is also readily soluble in  $\text{H}_2\text{T}$ ; in this latter respect it differs from the similarly formed  $\text{BiOCl}$  precipitate (156).

**193.** If a few drops of acid  $\text{SbCl}_3$  solution be poured upon a piece of platinum foil,<sup>1</sup> and a piece of  $\text{Zn}$  be dropped into it, a black deposit of  $\text{Sb}$  will rapidly form *on the foil*. If the foil be rinsed with water, and then boiled with  $\text{HCl}$ , the stain remains undissolved, but it is rapidly removed by boiling  $\text{HNO}_3$ .

#### TESTS DEPENDING ON THE FORMATION OF $\text{SbH}_3$ :

$\text{SbH}_3$  differs from  $\text{AsH}_3$  in not being poisonous, and in being free from smell.

**194.** If  $\text{SbH}_3$  gas, formed by the action of acid  $\text{SbCl}_3$  solution on  $\text{Zn}$ , is passed into  $\text{AgNO}_3$  solution in a precisely similar way to that described for  $\text{AsH}_3$  (181), a black precipitate ( $\text{SbAg}_3$ ) forms:



This precipitate is to be filtered off, and the filtrate, which will contain no  $\text{Sb}$ , rejected. Wash the precipitate four or five times with boiling water upon the filter; then pour upon it boiling dilute  $\text{H}_2\text{T}$  solution, which will

<sup>1</sup> A slip of platinum foil laid in a watch-glass or porcelain dish, or with turned-up edges, may be employed; the inverted lid of a platinum crucible is very convenient for this purpose.



dissolve the Sb, and receive the liquid in a test-tube; boil it, and pour it once more upon the filter; add HCl to the liquid, filter if necessary, and pass  $\text{H}_2\text{S}$  into it; orange-red  $\text{Sb}_2\text{S}_3$  will be precipitated.

195. A stain produced by Sb on porcelain, in the manner already described (182), differs from the As stain in presenting a *dead* surface and in being insoluble in  $\text{Na}_2\text{CO}_3$ ; also when the stain is dissolved by warming with  $\text{Am}_2\text{S}$ , the solution if gently evaporated leaves *orange-red*  $\text{Sb}_2\text{S}_3$ .

196. The Sb mirror, obtained as described in (183), differs from the As mirror by being formed much nearer to the flame, and on both sides of the heated part of the tube; it may further be distinguished by the tests given in (195). This mirror, after oxidation, is also insoluble in boiling water; and if dissolved in a little boiling HCl the solution gives an orange-red precipitate ( $\text{Sb}_2\text{S}_3$ ) when  $\text{H}_2\text{S}$  is passed into it, whereas the  $\text{As}_2\text{O}_3$  solution gives yellow  $\text{As}_2\text{S}_3$ .

196 *a*.  $\text{SbH}_3$  if allowed to act on filter-paper moistened with  $\text{HgCl}_2$  solution as described in 183 *a* for  $\text{AsH}_3$ , yields a *grayish-brown* stain.

197. Boiled with Zn or Al and  $\text{KHO}$ , no  $\text{SbH}_3$  is evolved. [Difference from As (184).]

198. If a little solid  $\text{KSbO}_3$  or  $\text{Sb}_2\text{O}_3$ , or any substance containing Sb, be mixed in a cavity on wood charcoal with  $\text{Na}_2\text{CO}_3$  and  $\text{KCy}$ , and the mixture be heated in the inner blowpipe flame, a white incrustation forms on the charcoal, and white globules of metallic Sb are obtained which are extremely brittle. The flame is colored pale green. If the melted Sb be allowed to stand aside on the charcoal the globule emits a white smoke, and coats itself with sharp white crystals of the oxide.

The two distinctive tests (199, 200) for antimonious and antimonie compounds given in the following table are seldom used; they may be read through<sup>†</sup> without trying the reactions, and may be referred to hereafter if required for analytical purposes.

DISTINCTIVE TESTS FOR ANTIMONIOUS AND ANTIMONIC  
COMPOUNDS.

Reagent.	Antimonious. (Use the above solution of $\text{SbCl}_3$ in dilute $\text{HCl}$ .)	Antimonic. (Use $\text{K}_2\text{Sb}_2\text{O}_7$ solution, obtained by boiling some "Potassium metantimonate" with $\text{H}_2\text{O}$ .)
199. Add excess of $\text{KHO}$ , then $\text{AgNO}_3$ solution.	A dark-colored precipitate which when shaken after addition of $\text{AmHO}$ leaves black $\text{Ag}_2\text{O}$ undissolved.	A brown precipitate, which dissolves entirely on addition of $\text{AmHO}$ .
200. Add excess of $\text{HCl}$ and warm; then pour in a little $\text{KI}$ solution:	No iodine is set free; proved by the liquid not turning brown and giving no color after being cooled and mixed with freshly prepared starch solution.	Iodine is liberated, giving a brown color to the liquid and yielding a deep-blue color when starch solution is added to the cold liquid.

TIN ( $\text{Sn}$ ).—Stannosum and Stannicum.

DISTINCTIVE REACTIONS FOR STANNOUS AND STANNIC  
COMPOUNDS.

Test.	Stannous Compounds. Use $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in dilute $\text{HCl}$ .	Stannic Compounds. Use $\text{SnCl}_4$ in dilute $\text{HCl}$ .
201. Pass $\text{H}_2\text{S}$ :	<i>Dark-brown precipitate</i> ( $\text{SnS}$ ): pour off two portions and show that the precipitate is soluble in $\text{KHO}$ and in <i>yellow</i> $\text{Am}_2\text{S}$ on heating; and is precipitated again by $\text{HCl}$ , from the $\text{KHO}$ solution as brown $\text{SnS}$ , from the $\text{Am}_2\text{S}$ solution as yellow $\text{SnS}_2$ . $\text{SnS}$ differs from $\text{SnS}_2$ in being insoluble in <i>colorless</i> $\text{Am}_2\text{S}$ , which readily dissolves $\text{SnS}_2$ .	<i>Yellow precipitate</i> ( $\text{SnS}_2$ ), often forming only when the liquid is heated; pour off portions and show that the precipitate is soluble in $\text{Am}_2\text{S}$ (both <i>yellow</i> and <i>colorless</i> ) and in $\text{KHO}$ on heating, and is precipitated again by $\text{HCl}$ as yellow $\text{SnS}_2$ from both solutions.
202. $\text{HgCl}_2$ :	<i>A white precipitate</i> ( $\text{Hg}_2\text{Cl}_2$ ): turns gray on being boiled if the $\text{SnCl}_2$ is in excess (145).	—
203. $\text{AuCl}_3$ : added after a few drops of $\text{SnCl}_4$ solution or of $\text{Cl}$ water:	<i>Purple or dark-brown precipitate</i> , "Purple of Cassius."	—

*Reactions common to Stannous and Stannic Compounds.*

204. Zn in presence of  $\text{HCl}$  precipitates from Sn solutions a spongy mass of Sn; the Zn and solution should be allowed to stand together for some time in a small porcelain dish; the action is much hastened by gentle heat. If this test is done on platinum foil the Sn is deposited in a spongy state *on the Zn and does not stain the Pt* (difference from Sb).  $\text{SnCl}_4$  is not so readily acted upon by Zn as  $\text{SnCl}_2$  is; from  $\text{SnCl}_2$  the Sn is often precipitated in beautiful crystals.

205. A solid Sn-compound,  $\text{SnCl}_2$  or  $\text{SnO}_2$ , mixed with powdered  $\text{Na}_2\text{CO}_3$  and  $\text{KCy}$ , and heated on charcoal in the inner blowpipe flame, gives a slight white incrustation and white particles of metallic Sn, which are with difficulty fused into globules. The globules of Sn differ from those of Pb by not marking paper (153).

## 206. GROUP II B.—TABLE OF DIFFERENCES.

The following tests answer for these elements in both sets of compounds; for distinctive tests see the preceding reactions.

Tests.	As.	Sb.	Sn.
<i>a. For liquids.</i>			
1. Pass $H_2S$ into the solution acidified with $HCl$ and heat; if no precipitate forms, heat to boiling, and again pass $H_2S$ :	Yellow precipitate, insoluble in boiling strong $HCl$ .	Orange-red precipitate, soluble in boiling strong $HCl$ .	$\left\{ \begin{array}{l} SnS - \text{Brown precipitate.} \\ SnS_2 - \text{Yellow precipitate.} \end{array} \right.$ Both soluble in boiling strong $HCl$ .
2. Zn and $HCl$ :	$AsH_3$ gas is evolved, which if passed into $AgNO_3$ solution gives a black precipitate of $Ag_2H_2AsO_3$ being left in solution; on adding dilute $AmHO$ to this solution yellow $Ag_3AsO_3$ precipitates.	$SbH_3$ gas is evolved, which if passed into $AgNO_3$ solution gives a precipitate of $Ag_3Sb$ , from which hot $H_2I^-$ solution dissolves $Sb$ ; $H_2S$ gives in this solution after adding $HCl$ orange-red $Sb_2S_3$ .	$Sn$ is deposited on the Zn strips.
3. Zn and $HCl$ on platinum:	$AsH_3$ evolved, no stain on the platinum.	Black stain of $Sb$ on the platinum.	$Sn$ deposited on the zinc, no stain on the platinum.
<i>b. For solids.</i>			
4. Heated with $Na_2CO_3$ and $KCy$ on charcoal in the inner blowpipe flame:	No metallic globules; smell of garlic.	Brittle metallic globules, white incrustation,	Malleable metallic globules, white incrustation.
5. Heated with solid $Na_2CO_3$ and $KCy$ in a bulb-tube:	Black mirror and smell of garlic.	—	—

The detection of any one member of this group is simple; the color of the precipitate with  $H_2S$ , confirmed by special tests, is quite sufficient to identify it with ease.

207. (s) *Many methods have been proposed for the sep-*

aration and detection of *As*, *Sb*, and *Sn*, when mixed; two of the most trustworthy are those introduced by *Hofmann* (208) and by *Fresenius* (210); a method more simple, though less trustworthy, is given in (209).

208. (s) *Hofmann's* method consists in pouring the solution into a flask in which *H* is being generated by the action of  $\text{HCl}$  upon *Zn*; *Sn* remains as a spongy mass on the *Zn*, *As* and *Sb* are evolved as  $\text{AsH}_3$  and  $\text{SbH}_3$ ; these gases, if passed into  $\text{AgNO}_3$  solution, yield soluble  $\text{H}_3\text{AsO}_3$  and insoluble  $\text{Ag}_3\text{Sb}$ , which are separated by filtration; the three members of this group thus separated are then detected by special tests.

*As*, *Sb*, *Sn*, occurring together in a solution, are tested for by precipitating them with  $\text{H}_2\text{S}$ , filtering, and testing the filtrate by passing  $\text{H}_2\text{S}$  through it as was directed for precipitating Group II A. The precipitate is then examined by Table II (435 *b*, Arsenic Group), using only the right-hand side of the table.

The  $\text{H}_2\text{S}$  precipitate may also be examined by the simpler method given in (209), or by the very accurate, but less simple method, in (210).

209. (s) The following method of examining a precipitate produced by  $\text{H}_2\text{S}$  for *As*, *Sb*, *Sn* is recommended by its comparative simplicity; it is sufficiently accurate for ordinary analyses where traces of these metals have not to be looked for. It depends upon the insolubility of  $\text{As}_2\text{S}_3$  in hot strong  $\text{HCl}$ , in which  $\text{SnS}$ ,  $\text{SnS}_2$ , and  $\text{Sb}_2\text{S}_3$  are soluble; the further separation of *Sb* and *Sn* is effected either by adding *Zn* alone to the acid solution, when *Sb* is evolved as  $\text{SbH}_3$  and *Sn* is deposited upon the *Zn*, or by adding *Zn* and *Pt*, when *Sn* is deposited on the *Zn* and *Sb* on the *Pt*.

The precipitate produced by  $\text{H}_2\text{S}$  is filtered off and allowed to drain for some time upon the filter in the funnel; it is best to drain it still further by carefully taking the filter out of the funnel, opening it out, and spreading it upon a piece of filter-paper folded several times upon itself; the precipitate is then removed to a small porcelain dish and heated for some time nearly to boiling with strong fuming  $\text{HCl}$ ; the liquid is cooled and filtered:



The residue will consist chiefly of  $As_2S_3$ , which is almost insoluble in strong  $HCl$ .

Dry the washed residue on the filter at a gentle heat, then mix it with three or four times as much powdered  $KCy$  and  $Na_2CO_3$ , and heat the mixture in a small bulb-tube, removing any drops of water inside the tube by a twisted piece of filter-paper; a black mirror (185):

*Presence of As.*

*Note.*—The  $As_2S_3$  may also be dissolved by heating with a little fuming  $HNO_3$ . The excess of  $HNO_3$  is boiled off and  $As$  detected as  $H_3AsO_4$  by adding  $AmCl$  excess of  $AmHO$  and  $MgSO_4$ ; or by addition of  $AgNO_3$ , and then cautiously neutralizing with  $AmHO$ .

The filtrate may be examined for  $Sb$  and  $Sn$  by either I or II below:

I. Place a piece of platinum foil in a porcelain dish and pour the acid filtrate upon it, then touch the foil with a piece of  $Zn$ ;  $H$  will come off with effervescence, and if either at once or after a few minutes a black stain appears upon the platinum, the *presence of Sb* is indicated.<sup>1</sup>

The platinum foil is removed and pieces of  $Zn$  are placed in the liquid; as soon as the bubbles of  $H$  cease to be given off,  $Zn$  still remaining undissolved, remove the pieces of  $Zn$ , rubbing and rinsing any dark deposit back into the dish; let this deposit settle, decant the liquid and heat the solid deposit with strong  $HCl$  for several minutes in a test-tube, dilute with a little water, filter if necessary, and add to the solution a few drops of  $HgCl_2$  solution; a white or gray precipitate (204, 202) indicates the *presence of Sn*.

II. The acid filtrate is poured into a little hydrogen flask (Fig. 34, p. 132), in which  $H$  has been coming off briskly for about five minutes, being produced by the action of a little strong  $HCl$  upon some pieces of  $Zn$ . The  $H$  is lighted at the jet, and the inside of a small porcelain dish or crucible lid pressed down upon the flame; a black stain not dissolved by hot  $Na_2Cl_2O$  solution shows the *presence of Sb*.

The residue in the flask is tested for  $Sn$ , as directed in the latter part of I (above).

**210.** (s) The following method of detecting  $As$ ,  $Sb$ ,  $Sn$ , described by Fresenius, is very delicate and trustworthy. It depends upon the fact that fusion with  $Na_2CO_3$  and  $NaNO_3$  converts  $As_2S_3$  into soluble  $Na_2HASO_4$ ,  $Sb_2S_3$  into insoluble  $Na_2H_2Sb_2O_7$ , and  $SnS_2$  into insoluble  $Sn$  or  $SnO_2$ .

The precipitated sulphides are dried on the filter and

<sup>1</sup> The  $Sb$  thus deposited on the  $Pt$  may, after rinsing the foil, be dissolved by heating the  $Pt$  in a test-tube with a little very dilute  $HNO_3$ ; on cooling, diluting, and passing  $H_2S$ , an orange-red precipitate will form, confirming the *presence of Sb*.

the precipitate<sup>1</sup> mixed well on a watch-glass or in an agate-mortar with equal weights of powdered  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$ ; this powder is dropped in small quantities at a time into some  $\text{NaNO}_3$  kept melted in a small porcelain crucible over a Bunsen flame. When the powder has all been added the crucible is heated sufficiently to keep the substance melted for a few minutes, and the melted mass is then poured into a small dry porcelain dish; as soon as the substance has cooled cold water is poured upon it in the dish and also upon the residue adhering to the inside of the crucible, and the solid substance is allowed to soak for some time, with occasional stirring, crushing it by pressure with a pestle if it does not easily fall to pieces; it is then filtered:

*The residue* is washed on the filter with a mixture of equal measures of water and alcohol, to prevent solution of the  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ , the washings are rejected. The precipitate is then rinsed into a small porcelain dish, using as little water as possible; a few drops of strong  $\text{HCl}$  are added and the dish is heated, more  $\text{HCl}$  being added, if necessary, to make the liquid acid to litmus-paper. Whether the residue has dissolved or not, place in the liquid a piece of clean platinum foil, and upon the foil a piece of pure  $\text{Zn}$ . If a black stain forms after a time upon the platinum, it proves the presence of  $\text{Sb}$ .<sup>2</sup> When the  $\text{Zn}$  ceases to be acted upon,  $\text{Sn}$  if present will remain as a spongy deposit. This is to be washed by decantation, dissolved by boiling with  $\text{HCl}$  in a test-tube, and  $\text{HgCl}_2$  added immediately to the solution; a white precipitate (202) shows the presence of  $\text{Sn}$ .

*Filtrate:*  $\text{HNO}_3$  is added until the solution is just acid after being boiled, then  $\text{AgNO}_3$  solution is poured in as long as it causes any precipitate, and very dilute  $\text{AmHIO}$  is added little by little.<sup>3</sup> A brown precipitate, readily dissolving in excess of  $\text{AmHIO}$ , shows the presence of  $\text{As}$ .

## GROUP I.—SILVER GROUP.

**211.** This group includes  $\text{Pb}$ ,  $\text{Ag}$ ,  $\text{Hg}'$  (Mercurous); its members differ from those of all the other analytical

<sup>1</sup> If the quantity of the precipitate is very small the part of the paper containing the precipitate is cut up into small pieces and treated as the precipitate.

<sup>2</sup> See the footnote on p. 142.

<sup>3</sup> Instead of mixing dilute  $\text{AmHIO}$  with the liquid, it may be carefully poured upon the top of the liquid; a brown color is then seen at the surface of contact.

groups by being precipitated as chlorides by  $\text{HCl}$ : since, however,  $\text{PbCl}_2$  is rather soluble in water,  $\text{Pb}$  is not entirely precipitated by  $\text{HCl}$ , and is usually found also in Group II A as  $\text{PbS}$ .

**LEAD (Pb).**—Reactions already given in Group II A (149-153).

**SILVER (Ag).**—Use  $\text{AgNO}_3$  solution.

**212.**  $\text{HCl}$ : white precipitate ( $\text{AgCl}$ ), becomes curdy on being shaken or heated: pour off into four tubes; filter one, wash the precipitate and let it stand for some time exposed to sunlight or common daylight, it will become blackish-purple; show with the other portions that  $\text{AgCl}$  dissolves readily when heated with  $\text{AmHO}$  or with  $\text{KCy}$  solution, and is precipitated again from these solutions on adding  $\text{HNO}_3$  in excess; also that it is insoluble in  $\text{HNO}_3$  even on boiling.

**213.**  $\text{H}_2\text{S}$  or  $\text{Am}_2\text{S}$ : black precipitate ( $\text{Ag}_2\text{S}$ ), insoluble in  $\text{Am}_2\text{S}$  or  $\text{KHO}$ , soluble in boiling dilute  $\text{HNO}_3$ .

**214.**  $\text{KHO}$ : brown precipitate ( $\text{AgHO}$ ), insoluble in excess.

**215.**  $\text{AmHO}$ : light-colored precipitate, produced only when *very dilute*  $\text{AmHO}$  is added drop by drop, easily soluble in excess of  $\text{AmHO}$ .

**216.** A mixture of a solid  $\text{Ag}$ -compound and powdered  $\text{Na}_2\text{CO}_3$  heated on charcoal, gives white malleable globules or scales of  $\text{Ag}$  and no incrustation.

**MERCUROSUM ( $\text{Hg}'$ ).**—Use  $\text{Hg}'_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  dissolved in dilute  $\text{HNO}_3$ .

Reactions (145, 146, 147, and 148) given under Mercuricum ( $\text{Hg}''$ ) yield precisely similar results with Mercuriosum ( $\text{Hg}'$ ), and may be repeated with  $\text{Hg}'_2(\text{NO}_3)_2$  solution.

In reaction (146), however, it is not necessary to add acid, since the  $\text{Hg}'_2(\text{NO}_3)_2$  solution is already acid.

**217.**  $\text{HCl}$ : a white precipitate ( $\text{Hg}'_2\text{Cl}_2$ ), insoluble in dilute acids unless warmed with both  $\text{HCl}$  and  $\text{HNO}_3$ , which convert it into soluble  $\text{Hg}''\text{Cl}_2$ : *becomes black when  $\text{AmHO}$  is poured upon it, but does not dissolve.*

218.  $AmHO$  or  $KHO$ : black precipitate, insoluble in excess.

219.  $Hg_2S$ : black precipitate ( $Hg'_2S$ ): this precipitate, like  $Hg''S$  (144), is insoluble in  $Am_2S$ , in hot strong  $HCl$ , and in hot strong  $HNO_3$ , but is easily dissolved when heated with a mixture of  $HNO_3$  and  $HCl$ .

## 220. GROUP I.—TABLE OF DIFFERENCES.

Tests.	Pb.	Ag.	Hg'.
<i>a. For liquids.</i>			
1. Add $HCl$ :	White precipitate soluble in boiling water; $AmHO$ neither dissolves the precipitate nor changes its color.	White curdy precipitate, insoluble in boiling water, easily soluble in warm $AmHO$ , reprecipitated from this solution by adding $HNO_3$ in excess.	White precipitate insoluble in boiling water, and insoluble in $AmHO$ , but blackened by it.
2. Add $AmHO$ :	White precipitate, insoluble in excess.	Brown precipitate, readily soluble in excess.	Black precipitate, insoluble in excess.
3. Add $K_2CrO_4$ :	Bright-yellow precipitate.	Chocolate-red precipitate.	Scarlet-red precipitate.
<i>b. For solids.</i>			
4. Fused with $Na_2CO_3$ on charcoal in the inner blowpipe flame:	White malleable globules of metal which mark paper; yellow incrustation on the charcoal.	White malleable globules or scales which do not mark paper; no incrustation.	No metallic globules.
5. Heated in a bulb-tube mixed with $Na_2CO_3$ :	—	—	Gray sublimate, consisting of globules of metallic mercury.

By the above differences any one member of this group is readily distinguished.

221. (s) *The separation and detection of Pb, Ag, and Hg', when mixed, depend upon:*

1st. The solubility of  $PbCl_2$  in boiling water, in which  $AgCl$  and  $Hg'_2Cl_2$  are insoluble.

2d. The solubility of  $AgCl$  in  $AmHO$ , in which  $Hg'_2Cl_2$  is insoluble.

The presence of each member, when thus separated, is then confirmed by one of its special tests.

**222.** (s) A solution which is to be examined for Pb, Ag, Hg', is precipitated by HCl added in excess, then filtered, and the clear filtrate is tested with more HCl to ascertain that no further precipitate is produced. The precipitate is then examined by Table I (433).

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The foregoing reactions only include those for the metals of common occurrence. For information concerning the detection and separation of the rarer metals, which will only be required by a somewhat advanced student, the appendix must be consulted. The metals gold and platinum, however, are briefly noticed here on account of their frequent employment for chemical and other purposes. These two metals are dissolved only by a mixture of HCl and HNO<sub>3</sub>; their most important reactions are given below.

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**GOLD (Au).—Use AuCl<sub>3</sub> solution.**

Gold solutions are usually bright yellow in color.

**223.** *SnCl<sub>2</sub>* containing a little *SnCl<sub>4</sub>*: purple or dark-brown precipitate ("Purple of Cassius"), best seen by performing the experiment in a white porcelain dish.

**224.** *FeSO<sub>4</sub>* produces either at once, or on heating the solution, a very finely divided precipitate of Au: the liquid usually appears bluish by transmitted light; always copper-red by reflected light:



**224 a.** *H<sub>2</sub>SO<sub>3</sub>* produces on boiling a similar precipitate of Au: by boiling the liquid for some time in a porcelain dish, the Au settles in small black masses, and the solution loses its color.

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**PLATINUM (Pt).—Use PtCl<sub>4</sub> solution.**

**225.** *AmCl* added to a strong solution produces on standing for some time, or more quickly on being stirred, a yellow precipitate (*Am<sub>2</sub>PtCl<sub>6</sub>*): rather soluble in hot water.

**226.** *SnCl<sub>2</sub>* gives a reddish-brown color in the solution acidified with HCl, owing to the formation of *PtCl<sub>2</sub>*:



The method of separating and detecting Au and Pt is fully stated in paragraphs 472-474.



\* \* *Note*.—Before commencing the reactions for acid-radicles the student may with advantage analyze several substances which are liable to contain any one or more of the members of the metallic groups. If only *one* metal has to be looked for (see column 1, paragraph 539), the directions given in paragraphs (330–369) may be followed, omitting those portions which relate to the detection of acid-radicles. If two or more metals may be present (see columns 2, 3, paragraph 539), full directions for ascertaining to which analytical group or groups they belong will be found in the General Table (419); and the group precipitate or precipitates thus obtained may be then examined by the group tables (433–439), with which the student will probably already be familiar.

### REACTIONS FOR ACID-RADICLES.

In the course of analysis acid-radicles are usually detected by special tests; they cannot advantageously be precipitated in groups and the members of each group then separated and identified, as is done in the case of metals. Accordingly the arrangement here adopted consists in simply placing together in a group such acid-radicles as in some respects resemble one another in their reactions, and at the end of each group stating upon what differences the detection of its members when occurring together depends.

The reactions for acid-radicles are worked through in a manner similar to that employed for the reactions of the metals,—a compound (usually a salt) containing the radicle being employed. At the end of each group the student may with advantage detect one or more of its members, as was done with the metals.

### GROUP 1.—SULPHATE GROUP.

Sulphates are the only commonly occurring salts which give with  $\text{BaCl}_2$  a precipitate insoluble in boiling  $\text{HCl}$ . Fluosilicates resemble sulphates in this respect, but differ in so many other reactions that they are considered hereafter (299–302) in connection with fluorides and silicates, to which they are more closely related.

SULPHATES ( $-''\text{SO}_4$ ).—Use  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

**227.**  $\text{BaCl}_2$  or  $\text{Ba}(\text{NO}_3)_2$ : white precipitate ( $\text{BaSO}_4$ ), insoluble when boiled with dilute  $\text{HCl}$  or  $\text{HNO}_3$ .

If  $\text{BaCl}_2$  or  $\text{Ba}(\text{NO}_3)_2$  be added to a solution containing much strong  $\text{HCl}$  or  $\text{HNO}_3$ , a white precipitate may be produced consisting of  $\text{BaCl}_2$  or  $\text{Ba}(\text{NO}_3)_2$ , which however is readily distinguished from the precipitate of  $\text{BaSO}_4$  by being dissolved when boiled with water.

$\text{Sr}(\text{NO}_3)_2$  and  $\text{Pb}(\text{NO}_3)_2$  give also white precipitates ( $\text{SrSO}_4$  and  $\text{PbSO}_4$ ).

**228.** *Blowpipe Test*.—Solid  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  or any solid sulphate, if mixed with solid  $\text{Na}_2\text{CO}_3^1$  and fused on charcoal in the inner blowpipe flame *produced from a spirit flame*, yields  $\text{Na}_2\text{S}$ :



The  $\text{Na}_2\text{S}$  is readily detected by detaching the solid mass, after it has cooled, from the charcoal with the point of a knife; placing a portion of it upon a bright silver coin, then moistening it with a drop of water and crushing it by pressure with a knife-blade. After the moistened mass has remained upon the coin for a short time rinse it off, a black stain will then be seen upon the silver where the substance had rested (231).

Another portion of the cool mass may be moistened with a drop of  $\text{HCl}$ , when the fetid smell of  $\text{H}_2\text{S}$  will be observed, and a piece of paper moistened with  $\text{PbA}_2$  solution and held above it, will be blackened (230).

This test for a sulphate is reliable only when it is known that sulphur in no other form is present in the substance to be tested; it is also necessary that no sulphur should be introduced in the  $\text{Na}_2\text{CO}_3$  or by the flame. Now coal-gas sometimes contains sufficient sulphur to give the above reaction with pure  $\text{Na}_2\text{CO}_3$ , hence it is always advisable to employ a spirit rather than a gas-flame.

*Hydrogen sulphate*, or *sulphuric acid* ( $\text{H}_2\text{SO}_4$ ), may be detected by producing black charred stains on paper which has been dipped into it and dried by heat; it also has a strong acid reaction to litmus, and evolves hydro-

<sup>1</sup> Addition of  $\text{Na}_2\text{B}_4\text{O}_7$  is useful in preventing the fused mixture from sinking into the charcoal.

gen with Zn, properties shown however by some metallic and acid sulphates.

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## GROUP II.—THE CARBONATE GROUP.

The five following classes of salts give off characteristic gases when acted upon by HCl.

\*\* The systematic tables of differences, such as are given for each group of the metals, are not drawn out for the acid-radicle groups; the student should have no difficulty in constructing such tables for himself, either mentally or on paper, by looking through the reactions.

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CARBONATES ( $-\text{CO}_3$ ).—Use  $\text{Na}_2\text{CO}_3$ , or white marble ( $\text{CaCO}_3$ ).

**229.** *HCl* or  $\text{H}\overline{\text{Cl}}$  or almost any other acid, if poured upon some  $\text{Na}_2\text{CO}_3$  in a test-tube, causes carbon-dioxide gas ( $\text{CO}_2$ ) to come off with effervescence; this gas is recognized by its property of turning lime- or baryta-water milky by the production in them of insoluble  $\text{CaCO}_3$  or  $\text{BaCO}_3$ .

The test may be tried in several ways:

1. The acid is poured upon the carbonate in a test-tube. A glass rod which has been dipped into some perfectly clear lime-water<sup>1</sup> and has a small drop adhering to its end is then introduced into the test-tube, carefully avoiding touching the liquid or the sides of the tube; the drop will quickly become milky.

2. The acid is poured upon the  $\text{Na}_2\text{CO}_3$  in a small beaker, and this is immediately covered with a watch-glass placed with its convex face downwards, having a drop of clear lime-water<sup>1</sup> adhering to the middle of the face; the drop becomes milky.

3. Since  $\text{CO}_2$  gas is much heavier than air, on adding acid the gas evolved from the carbonate will remain in the test-tube if the tube is held erect and its mouth loosely

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<sup>1</sup> Baryta-water gives a much more decided result than lime-water.

closed with the thumb; by gradually sloping the tube the heavy gas is poured into another test-tube containing lime-water<sup>1</sup> without allowing any liquid to flow out; on closing this tube with the thumb and well shaking it the lime-water will become milky; or if the inside of the tube has been rinsed with lime-water the sides become white.

4. The  $\text{CO}_2$ , if it is given off in considerable quantity, may also be made to pass into some lime-water through a doubly bent tube fitted air-tight by a perforated cork or india-rubber stopper into the tube in which the  $\text{CO}_2$  is generated, as shown in the Fig. 37; or the apparatus shown in Fig. 38 may be employed.

FIG. 37.



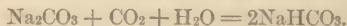
FIG. 38.



Of the above methods 1 and 3 are the most simple; by method 4 the  $\text{CO}_2$  is not found unless given off in somewhat large quantity.

The following precautions must be attended to. Since the milki-ness at first caused by  $\text{CO}_2$  disappears gradually when more  $\text{CO}_2$  is absorbed, if the lime-water does not at once become milky, it must be constantly watched to avoid the risk of its becoming milky and again clear before being seen.

Also if the addition of the first few drops of acid does not cause an effervescence of  $\text{CO}_2$  more acid should be added, as many carbonates retain the first portions of  $\text{CO}_2$  by forming acid carbonates:



A solid substance which is being tested by  $\text{HCl}$  for  $\text{CO}_2$  should be first moistened so as to drive out the air-bubbles entangled in it, which, in coming off, might make one suspect effervescence of  $\text{CO}_2$ .

*Hydrogen carbonate, or carbonic acid* ( $\text{H}_2\text{CO}_3$ ), can only exist in dilute aqueous solution; addition of lime-water to its solution causes milki-ness; but, since other substances in solution behave in a similar way, it is best found by boiling the liquid and passing the steam with the  $\text{CO}_2$  which accompanies it into lime-water; the lime-water becomes milky.

<sup>1</sup> Baryta-water gives a much more decided result than lime-water.

SULPHIDES (—S).—Use FeS for solid, and  $\text{Am}_2\text{S}$  for liquid.

230.  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  poured upon a small fragment of FeS causes  $\text{H}_2\text{S}$ -gas to come off with effervescence; this gas is detected by its fetid smell, resembling that of rotten eggs, and by its property of blackening  $\text{PbA}_2$ -solution by the formation of PbS. The gas may be made to act upon the  $\text{PbA}_2$ -solution by the methods given for  $\text{CO}_2$  (229), or better by placing a piece of filter-paper moistened with  $\text{PbA}_2$ -solution on the end of a glass rod so that one-half of the slip adheres to the glass rod and the other hangs free, and holding the rod in the gas as in the test for  $\text{CO}_2$  (229, 1).

This test is made much more delicate if the paper is moistened with a solution prepared by adding  $\text{KHO}$  to boiling  $\text{PbA}_2$ -solution until the precipitate first formed dissolves; a test-paper thus prepared becomes intensely blackened by  $\text{H}_2\text{S}$ .

231. Solutions of soluble sulphides, if dropped upon a bright silver coin, produce a black stain ( $\text{Ag}_2\text{S}$ ); this may be removed by rubbing the coin with moist lime.

232. Insoluble sulphides, which give off  $\text{H}_2\text{S}$  with  $\text{HCl}$  (*e. g.*, FeS) produce a black stain when placed on a silver coin and moistened with a drop of  $\text{HCl}$ .

233.  $\text{PbA}_2$ -solution gives with soluble sulphides a black precipitate (PbS). The solution produced by adding  $\text{KHO}$  in excess to  $\text{PbA}_2$ -solution is more delicate than  $\text{PbA}_2$  alone.

234. Many sulphides (*e. g.*,  $\text{FeS}_2$ , "Iron Pyrites"), and also free S, if strongly heated in a tube open at both ends, and held obliquely in the flame, or in the tube shown in Fig. 35 (p. 132), give off  $\text{SO}_2$ -gas, recognized by its pungent smell and by turning paper moistened with  $\text{K}_2\text{Cr}_2\text{O}_7$  green.

235. Reaction (306), given under  $\text{HCy}$ , may be employed also as a very delicate test for soluble sulphides. Test (228) for a sulphate, also answers for a sulphide.

*Hydrogen sulphide*, or *hydrosulphuric acid* ( $\text{H}_2\text{S}$ ), in aqueous solution, is easily recognized by (231) or (233), and, unless the solution is very dilute, also by its smell,

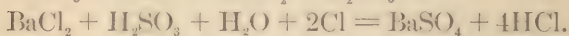


and by suspending lead-paper over the liquid:  $\text{H}_2\text{S}$ -gas is detected by (230).

SULPHITES ( $-\text{''SO}_3$ ).—Use  $\text{Na}_2\text{SO}_3$ .

236.  $\text{HCl}$ , or  $\text{H}_2\text{SO}_4$ , poured upon  $\text{Na}_2\text{SO}_3$  and warmed, gives off  $\text{SO}_2$ -gas, known by its pungent smell and by turning  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green; the  $\text{K}_2\text{Cr}_2\text{O}_7$  solution may be exposed to the gas by the methods described under (229), preferably by introducing a glass rod with a drop hanging upon its end into the gas; or by moistening a small strip of filter-paper with the  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and making it adhere by one-half of its length to the rod (230), the other half hanging freely, and introducing it into the gas as in (229, 1).

237.  $\text{BaCl}_2$ : white precipitate ( $\text{BaSO}_3$ ): entirely soluble in  $\text{HCl}$ , unless some  $\text{Na}_2\text{SO}_4$  is present, when  $\text{BaSO}_4$  remains undissolved; on adding  $\text{Cl-}$  or  $\text{Br-}$  water to the  $\text{HCl}$  solution,  $\text{BaSO}_4$  is formed and precipitated:



238.  $\text{Na}_2\text{SO}_3$ , added to a mixture of  $\text{HCl}$  and  $\text{Zn}$ , which is giving off pure  $\text{H}$ , immediately causes an evolution of  $\text{H}_2\text{S}$  with the  $\text{H}$ ; the  $\text{H}_2\text{S}$  is detected by its smell, or by blackening a piece of filter-paper moistened with solution of  $\text{PbO}$  in excess of  $\text{KHO}$  (230).

*Hydrogen sulphite*, or *sulphurous acid* ( $\text{H}_2\text{SO}_3$ ), can be found in aqueous solution by adding a drop of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, which will at once become green;  $\text{SO}_2$ -gas is found as directed under (236).

THEIOSULPHATES<sup>1</sup> ( $-\text{''S}_2\text{O}_3$ ).—Use  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .

239.  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  causes no immediate change in the cold; but the liquid on standing, or on being warmed, deposits a precipitate of yellow  $\text{S}$ , and  $\text{SO}_2$  is given off;

<sup>1</sup> Formerly known as hyposulphites.

the  $\text{SO}_2$  is recognized by its pungent smell and by changing the color of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution (236).

**240.**  $\text{Fe}_2\text{Cl}_6$ : gives a reddish-violet color, which vanishes after a short time, or immediately when heated, the  $\text{Fe}_2\text{Cl}_6$  solution at the same time loses its yellow color, owing to the change of  $\text{Fe}_2\text{Cl}_6$  into  $\text{FeCl}_2$ .

**240 a.**  $\text{AgNO}_3$ : a white precipitate ( $\text{Ag}_2\text{S}_2\text{O}_3$ ), becoming black after standing for a short time, or immediately upon being heated, owing to the formation of  $\text{Ag}_2\text{S}$ :



The above precipitate ( $\text{Ag}_2\text{S}_2\text{O}_3$ ) dissolves very readily in excess of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution, hence it is most easily obtained by dropping the latter into some  $\text{AgNO}_3$  solution.

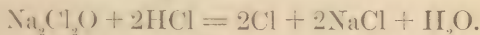
*Hydrogen theiosulphate*, or *theiosulphuric acid* ( $\text{H}_2\text{S}_2\text{O}_3$ ), is extremely unstable, rapidly separating into  $\text{S} + \text{H}_2\text{SO}_3$ .

**HYPOCHLORITES** ( $-\text{ClO}$ ).—Use  $\text{NaClO} \cdot \text{NaCl}$ , or  $\text{Na}_2\text{Cl}_2\text{O}$  solution.

Hypochlorites give off a faint smell of  $\text{Cl}$  in the air if solid or in strong solution.

**241.**  $\text{HCl}$ , or  $\text{H}_2\text{SO}_4$ , or even  $\text{H}_2\text{O}$  in the cold, or when gently warmed, if much water is present, sets free  $\text{Cl}$ -gas, which may be recognized by its smell, its yellowish color, and by bleaching a piece of moistened litmus-paper, which is held for a short time in the tube without touching the liquid or the sides of the tube.

A piece of litmus-paper shaken up with the solution, without addition of acid, is also bleached, the  $\text{CO}_2$  in the air probably liberating the  $\text{Cl}$ ; on addition of a drop of any acid the bleaching is very rapid:



**242.**  $\text{Pb}(\text{NO}_3)_2$ , or  $\text{PbA}_2$  solution, added in large quantity gives a white precipitate, becoming reddish, and then dark brown ( $\text{PbO}_2$ ) when boiled for a short time.

$\text{MnCl}_2$  likewise gives a *dark-brown* precipitate on heating.

*Hydrogen hypochlorite*, or *hypochlorous acid* ( $\text{HClO}$ ), is a yellow liquid with sweetish smell, which if strong is very unstable; it bleaches litmus, and evolves  $\text{Cl}$  when warmed with  $\text{HCl}$ .  $\text{Cl}_2\text{O}$ -gas is of a deep yellowish-green color, and has an irritating smell; it dissolves easily in water to form the above acid.

NITRITES ( $-\text{NO}_2$ ).—Use  $\text{KNO}_2$ .

243. Warmed with dilute  $\text{H}_2\text{SO}_4$ , reddish-brown "nitrous fumes," with a characteristic smell, are given off; they are best seen by looking down the tube at some white object.

244. If cold  $\text{FeSO}_4$  solution is added to  $\text{KNO}_2$  solution it becomes brown; on adding cold dilute  $\text{H}_2\text{SO}_4$  the color becomes much more intense; it is produced by the combination of  $\text{NO}$  with  $\text{FeSO}_4$ ; this color is destroyed by boiling, red fumes being given off (243).

245. If solution of  $\text{KI}$  and several drops of starch solution (par. 526, remark 35) are added to  $\text{KNO}_2$  solution, and the liquid is then made acid with  $\text{H}\bar{\text{A}}$ , an intense blue color will be produced, owing to the combination of iodine, set free by the  $\text{HNO}_2$ , with the starch; the experiment is best done in a white porcelain dish, the liquid, which often appears black at first, being diluted, if necessary, till its blue color becomes visible. This is a most delicate test, and is rather characteristic if the color is not produced till the  $\text{H}\bar{\text{A}}$  is added.

*Hydrogen nitrite*, or *nitrous acid* ( $\text{HNO}_2$ ) is extremely unstable, decomposing into  $\text{HNO}_3$ ,  $\text{NO}$ , and  $\text{H}_2\text{O}$ .

\* \* \* The student will have no difficulty in detecting any one of the above acid-radicles occurring singly in a liquid or solid: warming with  $\text{HCl}$  will usually indicate which of them is present, and its presence may then be confirmed by a second test.

246. (s) Most of the acids formed by the salts of Group II on addition of  $\text{HCl}$ , react upon one another; *e.g.*,  $\text{HClO}$  destroys  $\text{HNO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{SO}_3$ ; and  $\text{H}_2\text{S}$  destroys  $\text{H}_2\text{SO}_3$ . The analyst may often by skilful use of the

above reactions detect these acids when mixed, but their detection in certain mixtures is a problem only soluble by careful consideration, and not unfrequently insoluble.

$\text{SO}_2$ , if evolved, may be detected by  $\text{K}_2\text{Cr}_2\text{O}_7$  paper;  $\text{H}_2\text{S}$  by  $\text{PbA}_2$  paper;  $\text{Cl}$  by bleaching moist litmus-paper;  $\text{N}_2\text{O}_3$  by its brown color. But  $\text{CO}_2$  can only be detected in presence of much  $\text{SO}_2$  by passing the gases through hot  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, which absorbs  $\text{SO}_2$ ,  $\text{CO}_2$  passing on and being detected by lime-water.

### GROUP III.—NITRATE GROUP.

The two classes of salts which follow resemble one another in many respects, more particularly in the fact that no member of them is insoluble in water; hence no method of precipitating them is known.

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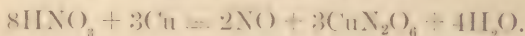
NITRATES ( $-\text{NO}_3$ ).—Use  $\text{KNO}_3$ .

247. Add to some  $\text{KNO}_3$  solution contained in a rather broad test-tube about an equal bulk of strong  $\text{H}_2\text{SO}_4$ ; cool the liquid by letting a stream of cold water run upon the tube from the tap; then hold the tube in a slanting position, and pour some strong cold  $\text{FeSO}_4$  solution in a gentle stream down the inside of the tube. If this solution is poured in with proper care it will form a distinct layer resting on the surface of the acid liquid, and at the surface of contact of the two layers a *dark-brown* film or ring will appear, sometimes extending upwards towards the surface of the liquid. The color is most easily seen by holding a piece of filter-paper between the tube and a bright flame or window, and looking through the tube at the light. A mere *yellow* color is often produced in the absence of a nitrate and may be disregarded.

The test is made more delicate by letting the tube stand in a small beaker of cold water for a few minutes, since heat prevents or destroys the brown color. If much nitric acid is present, on mixing the acid and  $\text{FeSO}_4$  solution by shaking, the brown color extends upwards,

until by the heat evolved by dilution of the acid the NO is expelled, forming brown fumes in the test-tube, and the liquid loses its dark-brown color (244).

248. Place some small scraps of Cu in some KNO<sub>3</sub> solution, and add strong H<sub>2</sub>SO<sub>4</sub>; brown nitrous fumes appear at once or on warming the tube; they are best seen, if small in quantity, by looking down the tube at a white surface. The liquid at the same time becomes blue from the presence in it of Cu(NO<sub>3</sub>)<sub>2</sub>:



NO is itself a colorless gas, but yields on mixture with air N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub> which are reddish-brown.

249. If some cold dilute indigo solution be poured into cold KNO<sub>3</sub> solution until it is decidedly blue, and then H<sub>2</sub>SO<sub>4</sub> be added, the blue color remains unchanged (difference from chlorates).

250. If any solid nitrate be fused for some time at a red heat with fusion mixture on platinum foil, oxygen gas is given off slowly with effervescence<sup>1</sup> and KNO<sub>2</sub> is formed; if the foil, after cooling, be boiled in water, a portion of the solution may be proved to contain KNO<sub>2</sub> by the test in paragraph (245); another portion, if acidified with HNO<sub>3</sub>, will be found to give no precipitate with AgNO<sub>3</sub> (difference from chlorates).

A solution of a nitrate may also be reduced to nitrate by nascent H. Add to a little KNO<sub>3</sub> solution some dilute H<sub>2</sub>SO<sub>4</sub> and starch paste with KI; no color will be produced, but on dropping in a fragment of Zn a deep-blue color is seen (245).

251. Solid KNO<sub>3</sub> fused on charcoal in the blowpipe flame "deflagrates," that is to say, the surface of the charcoal burns rapidly like gunpowder.

251 *a*. Many metallic nitrates [*e. g.*, Pb(NO<sub>3</sub>)<sub>2</sub>] when heated in a glass tube closed at one end, evolve reddish-brown fumes with a characteristic smell (N<sub>2</sub>O<sub>4</sub>) and oxygen—PbN<sub>2</sub>O<sub>6</sub> = N<sub>2</sub>O<sub>4</sub> + O + PbO.

<sup>1</sup> If this experiment is performed in a small hard-glass tube as described in (251), the oxygen can rarely be detected, since it is evolved very slowly; hence the student may perform the ignition on platinum foil and neglect the test for oxygen.



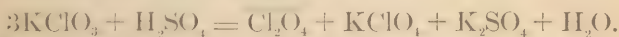
The fumes are recognized by their color and smell, the O by its inflaming a glowing splinter of wood.

*Hydrogen nitrate*, or *nitric acid* ( $\text{HNO}_3$ ), has a strong acid reaction; it gives with  $\text{FeSO}_4$  solution a brown ring (247), and with Cu brown fumes (248) without addition of  $\text{H}_2\text{SO}_4$ . Evaporated with quill-clippings, it stains them bright yellow.

CHLORATES ( $-\text{ClO}_3$ ).—Use  $\text{KClO}_3$ .

252. If to a *cold* solution of  $\text{KClO}_3$  some cold dilute indigo solution be added drop by drop till the liquid is colored faintly but distinctly blue, then some  $\text{H}_2\text{SO}_3$  or  $\text{NaHSO}_3$  be poured in and the mixture shaken, the blue color of the indigo is at once destroyed (difference from nitrates).

253. *Strong*  $\text{H}_2\text{SO}_4$  poured upon a little solid  $\text{KClO}_3$  becomes orange-red in color, and evolves when shaken a bright-yellow gas ( $\text{Cl}_2\text{O}_4$ ):

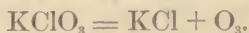


This gas has a smell somewhat resembling that of chlorine; it explodes readily when gently heated, hence on warming the mixture in the tube crackling sounds or small explosions will be produced. This experiment may be dangerous, unless the  $\text{KClO}_3$  is used in very small quantity, and heated gently with the mouth of the test-tube turned away from the operator.

254.  $4g.\text{NO}_2$  produces no precipitate with  $\text{KClO}_3$  solution if it is free from  $\text{KCl}$ . But if some solid  $\text{KClO}_3$ <sup>1</sup> be heated in a test-tube, or better in a small ignition-tube (10), after melting it begins to give off oxygen with effervescence; this gas may be recognized by placing in the tube a slip of wood with a spark at its end, which is easily obtained by kindling a match and suddenly blowing out the flame,—the spark is caused to burst into a flame. If the tube is then allowed to cool and the resi-

<sup>1</sup> If the chlorate used for this test does not yield a *soluble* chloride, fusion mixture must be mixed with it before heating, in order to obtain a soluble chloride in the residue.

due dissolved by boiling with some water, a portion of the solution will be found to give no reaction for  $\text{HNO}_2$  (245); but another portion will give a white precipitate ( $\text{AgCl}$ ) with  $\text{AgNO}_3$ , which does not dissolve in  $\text{HNO}_3$  even on boiling, but is easily soluble in  $\text{AmHO}$  (difference from a nitrate); this precipitate is caused by  $\text{KCl}$ :



**255. Blowpipe Test.**— $\text{KClO}_3$  if heated on charcoal in the blowpipe flame, causes the charcoal to “deflagrate.”

*Hydrogen chlorate*, or *chloric acid* ( $\text{HClO}_3$ ), is a colorless, odorless liquid, which first reddens and then bleaches litmus-paper; on being kept for some time it changes into  $\text{O}$ ,  $\text{Cl}$ ,  $\text{HClO}_4$  and  $\text{H}_2\text{O}$ ; the same change occurs rapidly when it is heated.

**256.** As will be seen, there is little difficulty in distinguishing a nitrate from a chlorate. When present together they more or less interfere with one another's reactions; but they may be detected, in the absence of chlorides and nitrites, by heating strongly for a short time and testing the residue for nitrite and chloride (250 and 254).

## GROUP IV.—CHLORIDE GROUP.

Chlorides, bromides, and iodides closely resemble one another; they are all precipitated by  $\text{AgNO}_3$  from solutions to which  $\text{HNO}_3$  has been added in excess; in this respect they differ from all salts except cyanides, ferrocyanides, and ferricyanides, and these are easily distinguished by other means.

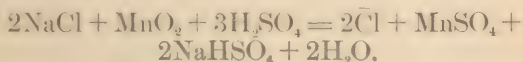
**CHLORIDES** ( $-\text{Cl}$ ).—Use  $\text{NaCl}$ .

**257.**  $\text{AgNO}_3$  added to a little  $\text{NaCl}$  dissolved in water, gives a *pure white* precipitate ( $\text{AgCl}$ ), which collects into curdy masses when heated or shaken, and quickly turns violet in sunlight or more slowly in daylight. Decant the water; to one portion of the precipitate add  $\text{HNO}_3$  and warm, it does not dissolve; to one other portion add  $\text{AmHO}$ , it readily dissolves. Decant the liquid from

a portion of the precipitate after shaking and letting the precipitate settle, and warm the precipitate with a little strong  $\text{H}_2\text{SO}_4$ , the acid remains colorless and no colored vapor is given off.

258. Solid  $\text{NaCl}$  warmed with strong  $\text{H}_2\text{SO}_4$  gives off colorless  $\text{HCl}$ -gas, which is recognized by fuming in the air, reddening moistened blue litmus-paper, and making a drop of  $\text{AgNO}_3$  solution on the end of a glass rod milky.

259. If solid  $\text{NaCl}$  be powdered and mixed with finely powdered  $\text{MnO}_2$ , then strong  $\text{H}_2\text{SO}_4$  added, and the mixture warmed, chlorine gas comes off:



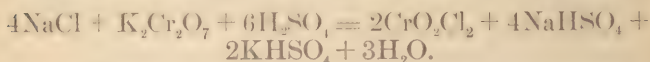
This gas is recognized by its property of bleaching a piece of moist blue litmus-paper, introduced into the tube on a glass rod. The most delicate way of testing is to warm the mixture in a small beaker covered with a watch-glass which bears on its under surface a piece of moist litmus-paper, and let the apparatus stand for some time. Moist starch is not colored when held in the air in the tube.

Many samples of commercial  $\text{MnO}_2$  evolve  $\text{Cl}$  when heated with  $\text{H}_2\text{SO}_4$ ; hence the  $\text{MnO}_2$ , unless specially prepared by precipitation, must be carefully tested before using it for this reaction; or the  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$  may be first boiled together as long as any bleaching action is produced when moist litmus is held in the tube, then the substance to be tested is added and  $\text{Cl}$  again tested for whilst heating the mixture.

260. If an intimate mixture of solid  $\text{NaCl}$  with three or four times as much  $\text{K}_2\text{Cr}_2\text{O}_7$  in fine powder be made by rubbing the two substances together in a mortar, and this mixture be then poured into the tubulated flask shown in Fig. 38,<sup>1</sup> page 150, and mixed with strong  $\text{H}_2\text{SO}_4$  by pouring in the acid and shaking it round

<sup>1</sup> The test-tube fitted as shown in Fig. 37 is much less suitable.

in the flask, on warming the flask reddish-brown vapor ( $\text{CrO}_2\text{Cl}_2$ ) will be evolved:



If the neck of the flask be closed by an india-rubber or a glass stopper, and the delivery-tube be made to dip into water in a test-tube, the vapor on passing into the water will impart to it a reddish-yellow color owing to the formation of  $\text{H}_2\text{CrO}_4$ :



On adding to this yellow liquid excess of  $\text{AmHO}$ , the color becomes pale yellow; on now adding excess of  $\text{HAc}$  the original reddish-yellow color is reproduced, and in this liquid the presence of  $\text{H}_2\text{CrO}_4$ , and therefore indirectly that of  $\text{HCl}$ , may be shown by the formation of a yellow precipitate on addition of  $\text{PbA}_2$  solution.

Since by this method the detection of a chloride depends on the formation of  $\text{H}_2\text{CrO}_4$  in the liquid in the test-tube from the vapor of  $\text{CrO}_2\text{Cl}_2$ , great care must be taken that no  $\text{H}_2\text{CrO}_4$  is introduced into that liquid from any other source. Now, since the mixture in the flask contains a chromate, the greatest precaution must be taken that none of it is allowed to get into the bent delivery-tube, and thence into the test-tube. In transferring the powder to the flask, it must be poured down the side of the *perfectly dry* neck opposite to that at which the delivery-tube enters; also, whilst heating the mixture it must not be allowed to rise or splash into the neck of the flask. If these precautions are not taken, and  $\text{H}_2\text{CrO}_4$  as such is introduced into the water in the test-tube, the test is worthless as an indication of the presence of a chloride.

Care must also be taken that the liquid is not sucked back from the test-tube into the flask. This is prevented by raising the delivery-tube out of the water in the test-tube as soon as the heating is stopped.

*Hydrogen chloride*, or *hydrochloric acid* ( $\text{HCl}$ ), is a colorless gas which fumes in the air, and dissolves very readily in water; both the gas and its solution render  $\text{AgNO}_3$  solution, which has been acidified with  $\text{HNO}_3$ , milky. Heated with  $\text{MnO}_2$  the liquid acid evolves chlorine gas.

BROMIDES (-'Br).—Use KBr.

261.  $AgNO_3$  added to a little KBr solution gives a *yellowish-white* precipitate ( $AgBr$ ), which is easily coagulated by heating or shaking the liquid; it is insoluble in  $HNO_3$ , but rather soluble in  $AmHO$ , thus somewhat resembling the  $AgCl$  precipitate, from which it is distinguished by its color. By shaking well, allowing to settle, decanting the liquid, and heating the precipitate with strong  $H_2SO_4$ , no violet vapor is evolved, the precipitate thus differing from  $AgI$ .

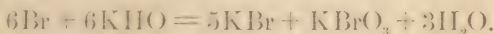
262. Solid KBr when heated with strong  $H_2SO_4$  gives off *reddish-brown* vapor of  $Br$ ,<sup>1</sup> which somewhat resembles  $Cl$  in smell, but differs by its color and by turning moist starch *orange-red*, the color disappearing by heat. This last test is best performed by dipping the wetted end of a glass rod into some powdered starch, and then moistening the adhering starch by breathing upon it several times. If  $MnO_2$  be mixed with KBr powder before adding  $H_2SO_4$ , the  $Br$  is evolved in greater quantity and more readily.

263. *Cl-water*, added carefully drop by drop to a little KBr solution whilst shaking it, liberates  $Br$ , which gives the solution an orange-red color; excess of *Cl-water* must be carefully avoided, as it destroys the color:



On warming a part of this solution in a dish, brown fumes are given off which color *orange-red* some starch held in the vapor as described in the preceding reaction.

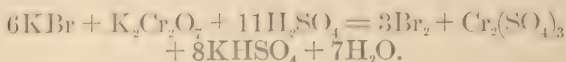
If  $CS_2$  be added to another portion and the liquids are then well shaken together, the  $Br$  is dissolved by the  $CS_2$ , and on standing the reddish-brown  $CS_2$  solution sinks to the bottom; on adding a little  $KHO$  solution and shaking well, the color of the  $Br$  again disappears from the  $CS_2$ , owing to the formation of the colorless salts  $KBr$  and  $KBrO_3$ :



<sup>1</sup> KBr solution does not so easily give off  $Br$  vapor, but the liquid becomes colored reddish-brown.



264. A mixture of solid  $\text{KBr}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  heated with strong  $\text{H}_2\text{SO}_4$  as in (260), gives off reddish-brown vapor of  $\text{Br}$ :



This vapor, if received in a little water, imparts its color to the water; if the liquid is shaken up with  $\text{CS}_2$ , however, the  $\text{Br}$  is dissolved away from the water by the  $\text{CS}_2$ , which forms a brown layer at the bottom of the water; by shaking well, after addition of  $\text{AmHO}$  or  $\text{KHO}$ , the color of the solution is destroyed (difference from a chloride).

*Hydrogen bromide*, or *hydrobromic acid* ( $\text{HBr}$ ), is a gas resembling  $\text{HCl}$ ; its solution differs by evolving  $\text{Br}$  when heated with  $\text{MnO}_2$ .

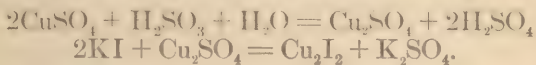
#### IODIDES (—I).—Use $\text{KI}$ .

265.  $\text{AgNO}_3$  added to a little  $\text{KI}$  solution, gives a yellow precipitate ( $\text{AgI}$ ), which is easily coagulated by heating or shaking the liquid; it is insoluble in  $\text{HNO}_3$ , and very slightly soluble in  $\text{AmHO}$ .

This precipitate differs from  $\text{AgCl}$  and  $\text{AgBr}$  by its color and its slight solubility in  $\text{AmHO}$ , but more particularly by its behavior when heated with strong  $\text{H}_2\text{SO}_4$ . If the precipitate, coagulated by heating or shaking the liquid, is allowed to settle and the liquid decanted, then strong  $\text{H}_2\text{SO}_4$  poured in and heated with the precipitate, the acid becomes colored red, and violet vapors of iodine are seen especially on looking down the tube; the color is particularly distinct after the tube has been allowed to cool for a short time. This vapor of iodine may be detected when almost invisible by holding in the air of the tube a glass rod previously dipped into freshly made starch solution, which will become colored blue.

266.  $\text{CuSO}_4$  mixed with  $\text{H}_2\text{SO}_3$  or  $\text{FeSO}_4$  solution, which reduces it to  $\text{Cu}_2\text{SO}_4$ , gives a white precipitate

( $\text{Cu}_2\text{I}_2$ ); warming, or the addition of a single drop of  $\text{AmHO}$ , causes this precipitate to form more quickly:



If this precipitate is allowed to settle and the water poured off, or if it be filtered, and the precipitate is then warmed with strong  $\text{H}_2\text{SO}_4$ , the liquid becomes violet and gives off violet fumes of  $\text{I}$ .

Solutions of chlorides and bromides are not precipitated thus by  $\text{Cu}_2\text{SO}_4$ .

**267.** Solid  $\text{KI}$  if warmed with strong  $\text{H}_2\text{SO}_4$ , gives off violet vapor of  $\text{I}$ ,<sup>1</sup> which, if in large quantity, cools on the sides of the tube to black solid: this vapor colors starch solution blue, as may be proved by dipping a rod moistened with freshly made starch solution<sup>2</sup> into it, or by pouring the heavy fumes out into a white porcelain dish whose inside has been wetted with starch solution, or by dipping into the vapor a slip of filter-paper moistened with starch solution. The  $\text{I}$  is more readily and plentifully evolved, if some  $\text{MnO}_2$  be mixed with the  $\text{KI}$  before adding  $\text{H}_2\text{SO}_4$ .

**268.** *Cl-water* added drop by drop, carefully avoiding excess which would form colorless  $\text{ICl}_3$ , sets free  $\text{I}$ , which dissolves in the water giving a brown liquid; divide this into three parts:

1. Heat one part; violet vapor of  $\text{I}$  is given off and is best seen by looking down the mouth of the tube at a white surface. The color is most distinctly seen if, before heating, some strong  $\text{H}_2\text{SO}_4$  is added to the liquid. If a glass rod is dipped into starch solution and held in the vapor, the starch becomes blue.

2. To another portion starch solution is added, which gives an intense blue color often appearing black unless much starch is added and the liquid largely diluted; on

<sup>1</sup>  $\text{KI}$  solution does not so easily give off purple vapor, but the liquid becomes reddish-brown or red.

<sup>2</sup> The starch solution must always be freshly made (par 526, remark 35), as after being kept it loses the property of yielding a blue color with iodine.

warming the solution the color disappears, but often reappears when the liquid is cooled. To insure the disappearance of the color on being heated, the solution must be diluted and the starch added in excess.

3. To the third portion add a drop of  $\text{CS}_2$  and shake well; the  $\text{CS}_2$  dissolves the I, and gradually settles to the bottom having a beautiful violet color. Add a little  $\text{KHO}$  solution and shake well, the violet color of the  $\text{CS}_2$  will disappear owing to the formation of the colorless salts  $\text{KI}$  and  $\text{KIO}_3$ .

The last two methods of testing for the free I are by far the most delicate known; but  $\text{Cl}$ -water is by no means the best reagent for setting I free from its compounds, because if added in excess it combines with the I and prevents its detection. The reagents described in (269) are much better suited for liberating I from its compounds.

269. If a little  $\text{KNO}_2$  is added to the  $\text{KI}$  solution, and then any dilute acid ( $\text{H}_2\text{A}$ ,  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ) poured in,  $\text{HNO}_2$  is produced and liberates I. A solution of  $\text{N}_2\text{O}_4$  in dilute  $\text{H}_2\text{SO}_4$ , made by heating  $\text{Pb}(\text{NO}_3)_2$  strongly and passing the red fumes into dilute  $\text{H}_2\text{SO}_4$  (528, 5), also sets free I from  $\text{KI}$ . The I thus liberated in solution may be identified by the three methods described in (268), of which the third is the most delicate.

These two reagents for liberating I do not hinder its detection if they are added in excess, and they are also useful because they do not liberate  $\text{Br}$  from its compounds.

270.  $\text{HgCl}_2$  gives with a solution of iodide a scarlet precipitate, with a solution of bromide or chloride it gives no precipitate;  $\text{PbA}_2$  gives with iodide solution a *bright-yellow* precipitate, with bromide or chloride a *white* precipitate.

*Hydrogen iodide*, or *hydriodic acid* (III), is a gas resembling  $\text{HCl}$  and  $\text{HBr}$ ; its solution differs by evolving I when heated with  $\text{MnO}_2$ .

271. A *chloride*, *bromide*, or *iodide* is easily detected by the foregoing tests. The reactions given in paragraphs (259) and (260) are perhaps the most characteristic tests for a chloride, those described in (262), (263)

and (264) for a bromide, whilst an iodide is detected with the greatest ease and certainty by reaction (269).

The color of the precipitate produced by  $\text{AgNO}_3$  in the solution made acid with  $\text{HNO}_3$ , and its behavior with  $\text{AmHO}$ , though less reliable than the above tests, serve to indicate which of these acid-radicles is present,  $\text{AgCl}$  being *pure white* and very easily soluble in  $\text{AmHO}$ ,  $\text{AgBr}$  being *pale yellow* and not readily soluble in  $\text{AmHO}$ , whilst  $\text{AgI}$  is *primrose-yellow* and almost insoluble in  $\text{AmHO}$ . See also the distinctive action of hot strong  $\text{H}_2\text{SO}_4$  on  $\text{AgI}$ , described in paragraph (265).

**272.** (s) *The detection of a chloride, bromide, and iodide when occurring together.*

The method of examination varies according to whether an iodide is present or absent; since a chloride cannot be detected in the presence of an iodide, the latter, if present, must be separated before proceeding to examine for the chloride (273). In paragraph (274) is given a process for detecting an iodide and bromide; it is of value only when a chloride has not to be tested for.

**273.** (s) To a small portion of the solution, made just acid if necessary by addition of dilute  $\text{H}_2\text{SO}_4$ , add a little cold freshly prepared starch solution and then strong  $\text{HNO}_3$ , or either of the reagents mentioned in (269), drop by drop; a dark-blue coloration<sup>1</sup> shows the *presence of an iodide*. The remainder of the solution is examined for a chloride and bromide by the directions given below under *A* or *B* according as an iodide is present or absent:

*A. An Iodide is Present.*—Add to the solution a reagent consisting of a mixture of  $\text{CuSO}_4$  solution with half its measure of strong  $\text{H}_2\text{SO}_4$  solution, and warm gently for a short time;  $\text{Cu}_2\text{I}_2$  will be precipitated (266). In order to be sure that the iodide is entirely precipitated, a small quantity of the liquid must be filtered and warmed with a little more of the above reagent; if any further precipitate is caused, the filtered portion is returned

<sup>1</sup> Black, unless the starch solution has been added in sufficient quantity to the dilute solution.

to the unfiltered liquid, more of the reagent is added to the whole, which is then warmed for a time and again tested as above, to see if the precipitation is complete; these trials are repeated until a small portion, on filtration, gives no further precipitate when warmed with more of the reagent. The whole is then filtered till clear, pure  $\text{NaHO}$  is added in excess to the filtrate and the liquid boiled. The precipitate thus produced is filtered off, and the filtrate, now free from iodide, is tested for bromide and chloride by the directions given under *B*.

*B. No Iodide is Present.*—Make the solution alkaline, if not already so, by addition of pure  $\text{NaHO}$ , then evaporate it to dryness in a porcelain dish, scrape the residue off the sides of the dish and mix it with three or four times as much powdered  $\text{K}_2\text{Cr}_2\text{O}_7$  by rubbing the two substances together in the dish with a pestle (260). Transfer this mixture into the small tubulated flask (Fig. 38, p. 150) by pouring it down the perfectly dry neck on the side opposite to that at which the tube enters, and taking the greatest care to let none of the powder enter the delivery-tube. Then pour into the flask strong  $\text{H}_2\text{SO}_4$  sufficient to cover the powder to the depth of about a quarter of an inch, at once close the neck with an india-rubber or glass stopper, and dip the end of the delivery-tube into water contained in a test-tube. Mix the contents of the flask by cautious shaking, and warm the mixture gently, carefully guarding against allowing any of the mixture to get into the delivery-tube and thence into the water in the test-tube.<sup>1</sup> As soon as no more reddish-brown vapor is visible in the flask or its delivery-tube, discontinue the heating, and immediately withdraw the test-tube. If no colored vapor has been evolved and the water in the test-tube is colorless, chloride and bromide are absent. If the water is colored, pour into it  $\text{CS}_2$  sufficient to form a layer at the bottom of the tube about as large as a small nut; close the mouth of the tube with the thumb, and shake vigorously; if the  $\text{CS}_2$  on

<sup>1</sup> See the precautions in the note at the end of par. 260.



settling shows a brown color, the *presence of Br from a bromide* is shown.

Separate the water from the  $\text{CS}_2$  by pouring it through a wetted filter, add to the filtrate  $\text{AmHO}$  in excess, then  $\text{HAc}$  in excess, and  $\text{PbAc}_2$  solution. A yellow precipitate indicates the presence of a chromate, which proves indirectly that a *chloride was present*.

273 a. (s) The above method will also serve for the examination for chloride, bromide, and iodide in the  $\text{AgNO}_3$  precipitate. The precipitate is dried, and fused for about ten minutes in a porcelain crucible with three or four times as much fusion mixture; the cool mass is boiled with  $\text{H}_2\text{O}$  for some time and filtered, the filtrate being examined as directed above (273).

274. (s) If only an iodide and a bromide have to be tested for, the following method may be employed. Pour into the solution  $\text{CS}_2$  sufficient to form a large drop at the bottom; add  $\text{Cl}$ -water drop by drop, shaking thoroughly after each addition: an iodide, if present, shows first by its liberated iodine coloring the  $\text{CS}_2$  purple, but on continuing the addition of  $\text{Cl}$ -water this color is destroyed; a bromide is then detected by a brown coloration of the  $\text{CS}_2$ , which, however, is also destroyed if too much  $\text{Cl}$ -water is added.

## GROUP V.—PHOSPHATE GROUP.

Phosphates and arsenates resemble one another closely in many reactions; the points of difference they present from one another and from other salts will, however, if carefully attended to, render their detection a simple matter.

PHOSPHATES ( $-\text{PO}_4$ ).—Use  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  solution.

275.  $\text{MgSO}_4$  solution to which some  $\text{AmCl}$  has been added and then a little  $\text{AmHO}$ , gives with  $\text{Na}_2\text{HPO}_4$  a white crystalline precipitate ( $\text{MgAmPO}_4$ ): this precipi-

tate is almost insoluble in  $\text{AmHO}$ , but easily soluble in acids. If very little  $\text{Na}_2\text{HPO}_4$  is present, the precipitate appears only on warming, stirring, or shaking well, and letting stand.

**276.**  $\text{Fe}_2\text{Cl}_6$  dropped in after a little  $\text{H}\bar{\text{A}}$  and some  $\text{Na}\bar{\text{A}}$  solution gives, especially when warmed, a yellowish-white precipitate of  $\text{Fe}'''\text{PO}_4$ .

**277.**  $\text{AmHMoO}_4$  dissolved in  $\text{HNO}_3$  gives a yellow precipitate if a drop of  $\text{Na}_2\text{HPO}_4$  solution is added to it; the formation of the precipitate is hastened by *gentle* warming, stirring, or shaking, but it often appears only after a time. Pour off a part of the liquid and show that the precipitate is soluble in  $\text{KHO}$ ,  $\text{NaHO}$ , and  $\text{AmHO}$ ; and insoluble in acids, especially in  $\text{HNO}_3$ .

This reaction (277), if properly performed, is the most delicate test known for a phosphate, but careful attention must be paid to the following precautions: The  $\text{AmHMoO}_4$  solution must be prepared according to the directions given in (526, remark 40). The solution to be tested must not be alkaline to test-paper; it is best made distinctly acid with  $\text{HNO}_3$ ; it is then to be added *in small quantity only* to some of the  $\text{AmHMoO}_4$  solution in a test tube, more of the liquid being added if after *gently* warming and stirring or shaking well no yellow precipitate forms after a few minutes. This last precaution must be particularly observed, as an excess of phosphate altogether prevents the formation of the precipitate: show that this is the case by pouring into some  $\text{Na}_2\text{HPO}_4$  solution, contained in a test-tube and made acid with  $\text{HNO}_3$ , a few drops of  $\text{AmHMoO}_4$  solution; it will be found that no precipitate will form even on heating and shaking the liquid, since the phosphate is present in large quantity compared with the  $\text{AmHMoO}_4$ ; but on adding a few drops of this liquid to some fresh  $\text{AmHMoO}_4$  solution the precipitate appears. It must also be remembered that  $\text{HCl}$  retards or prevents the formation of this precipitate, and therefore an  $\text{HNO}_3$  solution should always be used when possible.

**278.**  $\text{AgNO}_3$ : yellow precipitate ( $\text{Ag}_3\text{PO}_4$ ): pour off a portion, and show that the precipitate is soluble in  $\text{AmHO}$  and in  $\text{HNO}_3$ .

**278 a.** A very delicate test for the presence of P in the form of a phosphate or otherwise, consists in strongly heating the dry solid substance with a small piece of Na in a little tube of hard glass closed at one end: on breaking the tube and breathing upon the powdered substance a smell of onions, due to  $\text{H}_3\text{P}$ , is perceived.

A phosphate made into a paste with strong  $\text{H}_2\text{SO}_4$  and heated strongly at the tip of the inner blowpipe flame, gives a bluish-green color to the flame.

*Hydrogen phosphate*, or *phosphoric acid* ( $\text{H}_3\text{PO}_4$ ), is a colorless crystalline substance; its solution is strongly acid, but does not char paper and organic substances (difference from  $\text{H}_2\text{SO}_4$ ). It yields reactions (275 and 277).

ARSENATES ( $-\text{AsO}_4$ ).—Use  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$  solution.

279. The precipitates formed in reactions (275, 276, 277) for phosphates are precisely similar in appearance and general properties to those formed with the same reagents by arsenates. The precipitate, however, which is formed by an arsenate with  $\text{AgNO}_3$  differs from that given by a phosphate by being *brown* in color; also  $\text{AmHMoO}_4$  gives with an arsenate a precipitate *only on boiling*.

280. The following differences serve to detect and separate a phosphate and an arsenate:

1. The fact that an arsenate yields a precipitate with  $\text{AmHMoO}_4$  only when the liquid is *boiled*, whereas the corresponding precipitate with a phosphate is produced by *gentle heat*.

2. An arsenate solution, if boiled with strong  $\text{HCl}$ , gives when  $\text{H}_2\text{S}$  is passed into the hot liquid, first a white precipitate of  $\text{S}$ , then yellow  $\text{As}_2\text{S}_3$ ; a phosphate solution, under the same circumstances, gives no precipitate.

3. In a *perfectly neutral* solution,  $\text{AgNO}_3$  gives with an arsenate solution a *brown* precipitate, with a phosphate a *canary-yellow* precipitate.

Hence, if occurring separately, a phosphate and arsenate may be distinguished by one or more of these differences.

281. The simplest method of ascertaining which of these two acid-radicles is present is to throw the precipitate yielded by  $\text{AmCl}$ ,  $\text{AmHO}$ , and  $\text{MgSO}_4$  upon a filter, wash it with a little cold water, and drop  $\text{AgNO}_3$  upon it; if the precipitate consisted of  $\text{MgAmAsO}_4$  it will become *brown*, if of  $\text{MgAmPO}_4$  *canary-yellow* (280, 3). Or the precipitate produced by  $\text{AmCl}$ ,  $\text{AmHO}$ , and  $\text{MgSO}_4$  may be examined for arsenate by dissolving a part of it in dilute  $\text{HNO}_3$ , adding  $\text{AgNO}_3$  as long as it

causes any white precipitate, and then very dilute  $\text{AmHIO}$  gradually drop by drop; if arsenate is present a *brown* precipitate will form just before the liquid becomes alkaline to test-paper; phosphate gives a *yellow* precipitate. Instead of mixing the dilute  $\text{AmHIO}$  it may be poured upon the top of the acid liquid, when the color appears at the surface of contact.

282. *If both arsenate and phosphate have to be tested for*,  $\text{AmCl}$ ,  $\text{AmHIO}$ , and  $\text{MgSO}_4$  are added as long as any further precipitate is caused; the precipitate is filtered off<sup>1</sup> and dissolved in a little boiling strong  $\text{HCl}$ ,  $\text{H}_2\text{S}$  is passed for several minutes into this hot  $\text{HCl}$  solution, when the presence of arsenate is shown as above (280, 2); the precipitate, if any has formed, is filtered off and  $\text{H}_2\text{S}$  passed into the boiling filtrate; if any further precipitate is produced, the gas must be passed again until it no longer causes a precipitate; the clear filtrate from this precipitate is then evaporated just to dryness, dissolved in a little dilute  $\text{HNO}_3$ , and tested for phosphate by adding a few drops of it to  $\text{AmHMoO}_4$  solution and gently warming. Arsenite, if present, may be detected by  $\text{H}_2\text{S}$  in the filtrate from the  $\text{Mg}$  precipitate, acidified with  $\text{HCl}$ ; yellow  $\text{As}_2\text{S}_3$  is precipitated at once.

## UNGROUPED ACID-RADICLES.

The salts of the following acid-radicles present in their reactions no marked resemblances to one another or to other salts, and are usually detected by special tests.

BORATES ( $-\text{BO}_2$ , or  $-\text{BO}_3$ ).—Use  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

283. If some powdered  $\text{Na}_2\text{B}_4\text{O}_7$  be stirred with a little dilute  $\text{HCl}$  on a watch-glass and a strip of turmeric-paper

<sup>1</sup> A small portion of the precipitate may be filtered off upon another filter and tested at once for arsenate by dropping upon it  $\text{AgNO}_3$  solution. If the precipitate turns brown, arsenate is present and must be separated in the other part of the  $\text{Mg}$  precipitate before testing for phosphate; if the precipitate turns yellow, phosphate alone is present.

be half immersed in the liquid, then dried on a watch-glass in the steam-oven or on a water-bath,<sup>1</sup> the part which was moistened appears *reddish-brown*, and becomes *bluish-black* when moistened with  $\text{AmHO}$ . This is a most useful test for a borate.

284. If some methylated spirit be poured upon a little solid  $\text{Na}_2\text{B}_4\text{O}_7$  in a test-tube or porcelain dish, some strong  $\text{H}_2\text{SO}_4$  added, and the mixture be heated and set fire to, the spirit burns with a green-edged flame, seen best by blowing the flame out after it has burnt for a time and then relighting it. This test is not quite a characteristic, since some chlorides yield a somewhat similar green flame.

285. A mixture of  $\text{CaF}_2$ ,  $\text{Na}_2\text{B}_4\text{O}_7$ <sup>2</sup> and  $\text{KHSO}_4$ , if finely powdered, moistened, and heated on a loop of platinum wire in the inner blowpipe flame, colors the outer flame momentarily *green* after being heated for a short time.

This test is not always decisive, since many phosphates and Cu-salts give the same coloration, and it is besides liable to be masked by the flame colorations of other substances.

*Hydrogen borate*, or *boric acid* ( $\text{HBO}_2$ ), is a white porous mass; when combined with  $2\text{H}_2\text{O}$  it forms a crystalline scaly hydrate; when strongly heated these yield a fusible glass consisting of  $\text{B}_2\text{O}_3$ . The solution of the acid reddens litmus-paper and *colors turmeric reddish-brown, especially on drying the paper*. The acid is soluble both in  $\text{H}_2\text{O}$  and in alcohol; on evaporating these solutions, the acid passes off with the vapor of the liquid. Reactions (283, 284, 285) will serve to detect boric acid.

CHROMATES ( $-\text{CrO}_4$ ).—Use  $\text{K}_2\text{Cr}_2\text{O}_7$  (or  $\text{K}_2\text{CrO}_4$ ,  $\text{CrO}_3$ ) solution.

All chromates are more or less yellow or red in color. The yel-

<sup>1</sup> The paper may also be dried over a small flame, if it is not heated above steam-heat ( $100^\circ \text{C}$ .).

<sup>2</sup> Boric acid is better, since the Na flame coloration tends to conceal the green coloration caused by  $\text{BF}_3$ .

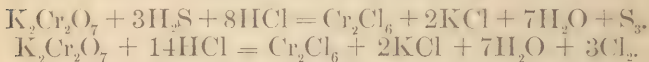


low solution of an alkaline chromate becomes orange-red on addition of an acid, owing to formation of a dichromate.

**286.** Various substances, which readily combine with oxygen, deoxidize acid  $K_2Cr_2O_7$  solution to a solution of a chromic salt, the color of the solution at the same time changing from *orange-red* to a *bright green*. To show this, add  $HCl$  or  $H_2SO_4$  to some  $K_2Cr_2O_7$  solution, divide the orange-red solution into five parts and deoxidize each of these portions by one of the following methods:

- a. Pass  $H_2S$  into the hot solution: white S separates.
- b. Add some  $NaHSO_3$  or  $H_2SO_3$  and warm.
- c. Add alcohol and boil.
- d. Boil for some time, after adding much strong  $HCl$ .
- e. Add some  $Zn$  to the acidified liquid and warm: the change of color is in this case slow.

In each case the change in composition is shown by the liquid becoming green; the following equations show the decomposition occurring with  $H_2S$  and with  $HCl$ , the others may be drawn out by the student:



This green solution gives all the reactions for  $Cr$  (102-104).

*Note.*—Since chromic acid is thus reduced by boiling with  $HCl$  and by  $H_2S$  to a chromic salt, a chromate leads to precipitation of  $Cr_2H_2O_6$  in Group III in the ordinary course of analysis.

*Hydrogen peroxide* ( $H_2O_2$ ), if added after some ether to an acid solution of a chromate, on well shaking the liquids cause the ether to assume a blue color; addition of a few drops of strong  $HNO_3$  is useful. The  $H_2O_2$  may be produced by adding  $BaO_2$  to the *cold* acid liquid. This reaction is extremely delicate and characteristic.

**287.**  $AgNO_3$ : *purple-red* precipitate ( $Ag_2CrO_4$ ): soluble in  $AmHO$  and in  $HNO_3$ .

**288.**  $PbA_2$ : *yellow* precipitate ( $PbCrO_4$ ): soluble in  $KHO$ , insoluble in  $HA$ .

289.  $BaCl_2$ : yellowish-white precipitate ( $BaCrO_4$ ): insoluble in  $H\bar{A}$ , soluble in  $HCl$ .

*Hydrogen chromate*, or *chromic acid* ( $H_2CrO_4$ ?).  $CrO_3$  dissolves in water to a reddish-yellow liquid, with a strongly acid reaction. The liquid evolves  $Cl$  and becomes green if it is boiled with  $HCl$ ; when neutralized by an alkali it becomes yellow, the solution yielding the reactions in pars. 287, 288, 289.

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SILICATES.  $\left\{ \begin{array}{l} \text{Use } Na_2SiO_3 \text{ solution for liquid; for} \\ \text{solid, finely ground sand or solid} \\ Na_2SiO_3. \end{array} \right.$

290.  $HCl$  added slowly drop by drop to a solution of  $Na_2SiO_3$  whilst stirring or shaking it, will usually, unless the solution is very dilute [see Note 2 below], give a gelatinous precipitate of  $H_4SiO_4$ ; but this precipitate is very apt to remain dissolved, hence its non-appearance is no proof of the absence of  $H_4SiO_4$ .

290 a. Small quantities of  $H_4SiO_4$ , or  $H_4SiO$  in dilute solution, may be detected by evaporating the solution, made acid with  $HCl$ , to dryness in a porcelain dish, and heating the residue to  $100^\circ$  as long as acid fumes come off: on stirring and warming the dry residue with strong  $HCl$ ,  $SiO_2$  remains undissolved as a white powder.

*Note 1.*—During the last part of the evaporation the silica often separates as a gelatinous mass, and unless the heat is lessened and the residue stirred with a glass rod it will spirt: spirting is best avoided by finishing the evaporation, as soon as the liquid becomes thick, upon a water-bath. The undissolved  $SiO_2$ , left on treating with  $HCl$ , is best seen by pouring out the liquid into a test-tube: it is soluble in hot  $KHO$  solution.

*Note 2.*—The solution of  $Na_2SiO_3$  used for these reactions is made of such a strength that acids do not precipitate  $H_4SiO_4$  from it, but by boiling some of it down to a quarter its volume before adding the acid the precipitate is usually obtained.

291.  $AmCl$  or  $Am_2(O)_3$  causes a gelatinous precipitate of  $H_4SiO_4$ , which usually forms only after a time.

*Blowpipe Tests.*

292. A little solid  $\text{SiO}_2$ , or a silicate, if fused into a bead of  $\text{Na}_2\text{CO}_3$ , causes frothing from  $\text{CO}_2$  escaping:



293. Fused in a bead of  $\text{NaAmHPO}_4$  the  $\text{SiO}_2$  is not dissolved, but floats about in transparent particles, and on cooling remains as little opaque masses in the bead. The particles of  $\text{SiO}_2$  are usually best seen in the bead whilst fused.

*Hydrogen silicate*, or *silicic acid* ( $\text{H}_4\text{SiO}_4$ ), is a white gelatinous substance with no reaction to litmus; it is insoluble in water, and but very slightly soluble in acids, but dissolves as an alkaline silicate in solutions of the alkalis or alkaline carbonates. On ignition it forms a white insoluble powder ( $\text{SiO}_2$ ), which yields reactions (292) and (293).

#### FLUORIDES (-F).—Use finely powdered $\text{CaF}_2$ .

The most useful tests for a fluoride depend upon setting free hydrofluoric acid and allowing this to act upon a glass surface, which it "etches" or corrodes, causing it to appear dim when perfectly dry.

294. *Strong  $\text{H}_2\text{SO}_4$* , if warmed with a little  $\text{CaF}_2$  in a test-tube, liberates  $\text{HF}$ , which causes the glass to behave towards the liquid as if it were greasy. The  $\text{HF}$  etches the glass, and on washing away the cooled mixture, and perfectly drying the inside of the tube, it will be found to be dimmed and roughened.

This test is often performed by gently warming the substance, upon which several drops of strong  $\text{H}_2\text{SO}_4$  have been poured, upon a watch-glass for some time; on washing off the substance and drying the glass thoroughly it will be found to be dimmed and roughened where the substance and acid rested; this is best seen, if only very slight, by holding the glass so as to see the reflection from its surface.

295. A less simple, but more delicate plan, consists in placing the  $\text{CaF}_2$  in a platinum crucible, or in a small leaden cup made by bending a piece of sheet-lead, and

pouring upon it some strong  $\text{H}_2\text{SO}_4$ . The crucible is then covered with a watch-glass, with its hollow upwards, and filled with cold water to keep the glass cool; the crucible is placed in a porcelain dish containing sufficient hot water to reach half way up the sides of the crucible, the water being occasionally heated if necessary by a small flame;<sup>1</sup> on removing the watch-glass after ten minutes or more, washing and then thoroughly drying it, the part of the surface covering the crucible will be found to be dimmed by the action of the  $\text{HF}$  vapors. The delicacy of this method is much increased by the modification described in (296).

296. The convex surface of a watch-glass is covered with a thin film of beeswax or solid paraffin by carefully heating the glass held by crucible-tongs at some distance above a flame, then rubbing its convex side with a piece of wax or paraffin; it is thus covered with a melted layer, which may be made uniform by once more heating the glass, allowing any excess of wax to drop off, and keeping the glass moving whilst it cools; the coating is finally hardened by immersion for a short time in cold water. Lines or characters are then traced on the glass towards its centre by gentle pressure with the point of a penknife, the object being simply to remove the wax from these parts and not to scratch the glass. The glass thus prepared is exposed as in (295) to the  $\text{HF}$  vapor for about twenty minutes or half an hour, the wax being prevented from melting by cold water in the hollow of the glass. The watch-glass is then removed and cleansed from wax by holding it with crucible-tongs above the flame and quickly wiping off the wax when melted: a clean bright surface will be thus obtained on which the traced lines will usually be visible at once on holding the glass up to the light; but if mere traces of a fluoride were present they will be made visible by breathing upon the cold surface.

297. The presence of  $\text{SiO}_2$  or a silicate prevents the

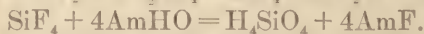
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<sup>1</sup> Or the crucible may be heated *gently* over a very small flame or on a sand-bath.

liberation of HF by  $\text{H}_2\text{SO}_4$ ,  $\text{SiF}_4$  being given off instead: this gas possesses no etching power, and therefore if  $\text{SiO}_2$  or a silicate is present, the methods given above do not serve for the detection of a fluoride.  $\text{SiF}_4$ , however, produces white fumes in air, and if passed into dilute AmHO yields a colorless flocculent precipitate of  $\text{H}_4\text{SiO}_4$  and gives AmF in solution: the formation of the flocculent precipitate of  $\text{H}_4\text{SiO}_4$  is sufficient proof of the presence of a fluoride, but the AmF itself may be detected in the filtrate from this precipitate by adding  $\text{CaCl}_2$ , filtering off the precipitate of  $\text{CaF}_2$ , and drying and examining it by (296).

By mixing  $\text{SiO}_2$  with any substance to be tested for a fluoride the above method may be employed for its detection; use for the reaction a mixture of  $\text{CaF}_2$  and  $\text{SiO}_2$ . A small piece of marble may be dropped into the tube in which the  $\text{SiF}_4$  is evolved, to carry that gas over into the AmHO solution.

The changes which occur are thus expressed:



298.  $\text{CaCl}_2$  added to NaF solution<sup>1</sup> gives a gelatinous almost transparent precipitate ( $\text{CaF}_2$ ), which becomes more visible on heating or adding AmHO: slightly soluble in HCl, almost insoluble in HA.

*Hydrogen fluoride*, or *hydrofluoric acid* (HF), is a colorless gas, which fumes in the air, etches glass, and dissolves easily in water. The solution of HF is acid in reaction, and differs from all other acids in dissolving SiO and attacking insoluble silicates.

FLUOSILICATES ( $-\text{SiF}_6$ ).—Use  $\text{H}_2\text{SiF}_6$ .

299.  $\text{BaCl}_2$ : white precipitate ( $\text{BaSiF}_6$ ), which usually appears only on gently warming the solution, and thus

<sup>1</sup> Prepared by boiling in water the mass obtained by fusing for several minutes on platinum foil some powdered  $\text{CaF}_2$  and fusion mixture, filtering the solution, and acidifying the filtrate with HA.



differs from  $\text{BaSO}_4$ : it is somewhat soluble in boiling  $\text{HCl}$ , but insoluble in alcohol. Put by some of this precipitate for reaction (301).

This precipitate differs from the precipitate of  $\text{BaSO}_4$ , which it somewhat resembles in being rather insoluble in  $\text{HCl}$ , by being more or less transparent and crystalline; but fluosilicates differ from sulphates also in giving no precipitates with  $\text{Sr NO}_3\frac{1}{2}$  or  $\text{Pb(NO}_3)_2$ , and in giving, when heated with excess of  $\text{AmHO}$ , a flocculent precipitate of  $\text{H}_4\text{SiO}_4$ , and  $\text{AmF}$  in solution (297); fluosilicates differ also by the following very distinctive reactions.

**300.**  $\text{KCl}$ , on warming, gives a very transparent gelatinous precipitate ( $\text{K}_2\text{SiF}_6$ ), which is visible only after being allowed to settle for a time; it is insoluble in alcohol.

**301.** By evaporating  $\text{H}_2\text{SiF}_6$  solution, or heating a fluosilicate, with strong  $\text{H}_2\text{SO}_4$ ,  $\text{HF}$  is given off, and may be detected by its etching action on glass (294 *et seq.*).

Evaporate a little  $\text{H}_2\text{SiF}_6$  or  $\text{BaSiF}_6$  from (299), after adding strong  $\text{H}_2\text{SO}_4$ , upon a watch-glass to dryness; on washing off the residue the glass will be found to be etched.

**301 a.** A solid substance (*e. g.*, the precipitate of  $\text{BaSiF}_6$  or  $\text{K}_2\text{SiF}_6$ ) may also be examined by any of the methods given above for  $\text{HF}$ , the most delicate being (296). This method is particularly useful for proving a precipitate produced by  $\text{BaCl}_2$  to consist of  $\text{BaSiF}_6$ .<sup>1</sup>

**302.** The above reactions readily distinguish between sulphates and fluosilicates, both of which give precipitates with  $\text{BaCl}_2$ , which are insoluble in boiling  $\text{HCl}$ . There is only one other class of salts—the selenates—which give with  $\text{BaCl}_2$  a white precipitate insoluble

<sup>1</sup> The readiest means of producing an etch with this precipitate is to pour it off into a watch-glass, decant the water, and warm the precipitate for some time with strong  $\text{H}_2\text{SO}_4$ ; on washing the glass and drying it, it will be found to be corroded. When the more delicate process (296) has to be employed, the precipitate should be shaken up with the liquid, poured off into a platinum crucible or leaden cup, the liquid decanted, and the precipitate warmed with strong  $\text{H}_2\text{SO}_4$  as described in (296).

in HCl, and this precipitate ( $\text{BaSeO}_3$ ), if boiled with strong HCl for some time, evolves Cl and gradually dissolves as  $\text{BaSeO}_3$ , thus differing from  $\text{BaSO}_4$  and  $\text{BaSiF}_6$ ; further, this HCl solution, if warmed with  $\text{H}_2\text{SO}_3$ , yields a reddish precipitate of Se.

*Hydrogen fluosilicate*, or *hydrofluosilicic acid* ( $\text{H}_2\text{SiF}_6$ ), is a strongly acid liquid, volatilizing entirely as  $2\text{HF} + \text{SiF}_4$  when heated in platinum. By evaporating it in glass the glass is etched. It is precipitated by KCl and by  $\text{BaCl}_2$ .

### REACTIONS OF ORGANIC ACID-RADICLES.

The following acid-radicles are included here, although the first four are frequently, and the other three always, classed amongst organic compounds, because they are of such frequent occurrence, and their detection is usually a matter of so little difficulty that they may reasonably be appended even to an elementary treatise on inorganic analysis.

#### CYANIDES ( $-\text{Cy}$ ).—Use KCy solution.

KCy smells of bitter almonds; the alkaline cyanides also smell faintly of the same.

303.  $\text{AgNO}_3$ : white precipitate ( $\text{AgCy}$ ), most easily obtained by pouring a drop of the KCy solution into the  $\text{AgNO}_3$  solution: show with three separate portions that this precipitate is soluble in KCy solution added in excess, and in AmHO, but insoluble in dilute  $\text{HNO}_3$ .

If some of the precipitate be filtered off and well washed with hot water until free from  $\text{AgNO}_3$  (shown by HCl causing no milkiness with the last few drops of the washing water), then dried, scraped from the filter into a porcelain crucible, and heated strongly, Ag is left; if this residue on cooling be warmed with a little dilute  $\text{HNO}_3$ , it dissolves, giving off red fumes; and a drop of HCl added to this solution gives a curdy precipitate of  $\text{AgCl}$ . This reaction distinguishes  $\text{AgCy}$  from  $\text{AgCl}$ ,  $\text{AgBr}$ , and  $\text{AgI}$ , which like it are precipitated by

$\text{AgNO}_3$ , and are insoluble in  $\text{HNO}_3$ , but which, when dried and strongly heated, melt without decomposing; hence, after cooling, if  $\text{HNO}_3$  be warmed with them it dissolves out no Ag, and  $\text{HCl}$  added to the  $\text{HNO}_3$  gives either no precipitate or a mere milkiness due to imperfect washing of the precipitate.

This method is somewhat tedious and need seldom be used, cyanides being readily detected by the following reactions.

**304.** If some  $\text{FeSO}_4$  solution, mixed with several drops of  $\text{Fe}_2\text{Cl}_6$ , is added to  $\text{KCy}$  solution and the liquid is then made strongly alkaline with  $\text{KHO}$  and boiled, then cooled and  $\text{HCl}$  added to acid reaction, "Prussian blue" ( $\text{Fe}'''_4(\text{Cy}_3)^1$ ) remains as a deep-blue precipitate; or, if in small quantity, it dissolves, giving a bluish-green solution. If no cyanide had been present, the addition of  $\text{HCl}$  would have given a nearly colorless liquid.

**305.** If to some  $\text{KCy}$  solution, contained in a test-tube fitted as shown in Fig. 37 (p. 150), dilute  $\text{H}_2\text{SO}_4$  is added, then a small piece of marble dropped in and the liquid boiled, allowing the steam to pass off into some  $\text{Am}_2\text{S}$  solution,  $\text{AmCyS}$  is formed. This substance gives with  $\text{Fe}_2\text{Cl}_6$  a *blood-red* coloration, which may be obtained by pouring the  $\text{Am}_2\text{S}$  solution out into a porcelain dish, boiling it, allowing it to cool, making acid with  $\text{HCl}$  (see Note 1, p. 180), and adding several drops of  $\text{Fe}_2\text{Cl}_6$ ; a blood-red color, only faintly seen when but little  $\text{KCy}$  is used, shows that  $\text{HCy}$  has passed into the  $\text{Am}_2\text{S}$ , producing  $\text{AmCyS}$ , and therefore proves the presence of a cyanide.

A little of this red liquid should be added to some  $\text{HgCl}_2$  solution; if the red color is destroyed it was certainly due to the presence of  $\text{AmCyS}$ .

The marble is used to cause evolution of  $\text{CO}_2$ -gas, which lessens the risk of the  $\text{Am}_2\text{S}$  being sucked back during the reaction.

**306.** The former test can often be more simply performed by boiling the solution of  $\text{KCy}$  or  $\text{HgCy}_2$  with  $\text{Am}_2\text{S}$ , which must be added until the yellow color remains after boiling for a short time. If a dark-colored precipitate forms, this must usually be filtered off before

<sup>1</sup> The symbol  $\text{Cy}$  conveniently represents the group  $(\text{FeCy}_6)^1$ ; it is used here to avoid brackets.

the color of the filtrate can be seen. Then filter if necessary, acidify with  $\text{HCl}$  in a porcelain dish (see Note 1, below), and add  $\text{Fe}_2\text{Cl}_6$  in small quantity; a blood-red color is produced in the liquid, which is not removed by heat or addition of  $\text{HCl}$ , but may be destroyed by adding a few drops of the liquid to some  $\text{HgCl}_2$ .

*Note 1.*—On adding  $\text{HCl}$  to the  $\text{Am}_2\text{S}$  (305, 306), white  $\text{S}$  separates unless the yellow liquid has been previously boiled in a porcelain dish until it becomes colorless, filling in distilled water as it evaporates; but this separation of  $\text{S}$  is advantageous, since it helps to show by its whiteness even a faint reddish tint in the liquid. Methods (304, 305, 306) are exceedingly delicate tests for a cyanide. Methods (305) and 306, if less readily performed than (304), exceed it in delicacy. Method (306) is the more easy of the two to perform, and (305) is only used in cases where, after boiling with excess of  $\text{Am}_2\text{S}$ , the filtrate is dark-colored, and therefore the red coloration would be invisible.

*Note 2.*— $\text{HgCy}_2$  does not show the reactions for a cyanide by methods (303, 304, and 305); but by boiling with  $\text{Am}_2\text{S}$ , according to method (306),  $\text{AmCyS}$  is obtained in the filtrate from the black  $\text{HgS}$  precipitate, and will give the red coloration with  $\text{Fe}_2\text{Cl}_6$ .

Solid  $\text{HgCy}_2$  heated in a small tube closed at one end also gives off cyanogen gas, which burns with a peachblossom-colored flame.

*Hydrogen cyanide*, or *hydrocyanic* ("Prussic") acid ( $\text{HCy}$ ), is a colorless, volatile, inflammable liquid, smelling like bitter almonds: it is *highly poisonous*, both when inhaled as vapor and swallowed as liquid: it readily mixes with water. The acid is easily detected by  $\text{AgNO}_3$  (303), also by (304), or by formation of  $\text{AmCyS}$  when the liquid is boiled with  $\text{Am}_2\text{S}$  (306).

FERROCYANIDES ( $-\text{FeCy}_6^1$  or  $-\text{Cfy}_6$ )—Use  $\text{K}_4\text{FeCy}_6 \cdot 3\text{H}_2\text{O}$  (or  $\text{K}_4\text{Cfy}_6 \cdot 3\text{H}_2\text{O}$ ) solution.

**307.**  $\text{Fe}_2\text{Cfy}_6$ : dark-blue precipitate, "Prussian blue" ( $\text{Fe}_4\text{Cfy}_3$ ): insoluble in  $\text{HCl}$ , soluble in  $\text{H}_2\text{C}_2\text{O}_4$  to a dark-blue liquid: changed by  $\text{KHO}$  into brown  $\text{Fe}_2\text{Ho}_6$ .

<sup>1</sup> This part of the formula of a ferrocyanide is conveniently written  $\text{Cfy}$  to avoid using brackets.

The solubility in  $H_2\bar{O}$  and insolubility in  $HCl$  are shown by pouring off portions, heating them with  $HCl$  and  $H_2O$  respectively, filtering and noting whether the filtrate is blue: a third portion is mixed with  $KHO$ , and becomes brown.

**308.**  $FeSO_4$ : light-blue precipitate ( $Fe''K_2\bar{Cfy}$ ), which quickly becomes darker on standing in the air, or immediately on addition of  $Cl$ -water or  $Br$ -water, or on warming with  $HNO_3$ : it is insoluble  $HCl$ .

**309.**  $CuSO_4$ : a chocolate-colored precipitate ( $Cu''_2\bar{Cfy}$ ), insoluble in  $H\bar{A}$ .

**310.**  $AgNO_3$ : white precipitate ( $Ag_4\bar{Cfy}$ ), insoluble in  $HNO_3$  and in  $AmHO$ . If heated with  $HNO_3$  this precipitate changes to orange-red  $Ag_6\bar{Cfy}_2$ , soluble in  $AmHO$ .

FERRICYANIDES [ $-^{vi}(FeCy_6)_2$ , or  $-^{vi}\bar{Cfy}_2$ ]. — Use  $K_6(FeCy_6)_2$  (or  $K_6\bar{Cfy}_2$ ) solution.

**311.**  $Fe_2Cl_6$ : dark-green or brown coloration; no precipitate is formed, as may be seen by adding much water to the liquid.

**312.**  $FeSO_4$ : dark-blue precipitate, "Turnbull's blue," ( $Fe''_3\bar{Cfy}_2$ ): insoluble in acids: blue color destroyed by  $KHO$ .

**313.**  $CuSO_4$ : yellowish precipitate.

**314.**  $AgNO_3$ : orange-colored precipitate ( $Ag_6\bar{Cfy}_2$ ), insoluble in  $HNO_3$ , soluble in  $AmHO$ . Frequently a white residue is left on adding  $AmHO$ , consisting of  $Ag_4\bar{Cfy}$ , and showing that  $K_4\bar{Cfy}$  was present in the  $K_6\bar{Cfy}_2$  solution.

SULPHOCYANIDES ( $-^iCyS$ ).—Use  $KCyS$  solution.

**315.**  $Fe_2Cl_6$ : blood-red coloration, but no precipitate: the color is destroyed by  $HgCl_2$  solution, but not by  $HCl$ .

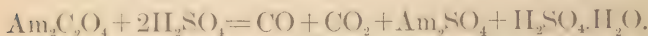


**316.** Cyanides are usually detected in analysis by methods (304, 305, 306). Ferro- and ferricyanides can be found and distinguished by their first three tests, or by the precipitate given by  $\text{AgNO}_3$  in the solution acidified with  $\text{HNO}_3$ ; this precipitate, if a ferricyanide is present, will have a more or less decided orange-red color; on filtering, or decanting, and warming the precipitate with  $\text{AmHIO}$ , white,  $\text{Ag}_4\text{Cty}$  will be left if a ferrocyanide was present, and on acidifying the filtrate with  $\text{HNO}_3$  orange-red  $\text{Ag}_6\text{Cty}_2$  will be precipitated. A sulphocyanide is found by (315).

The three following acid-radicles and their salts differ from the foregoing by being charred and emitting a smell of burning when heated in the solid state; oxalates, however, do so only to a slight extent. If the salt be one of the alkalies or of the alkaline earths, the residue left after ignition contains a carbonate, which effervesces with an acid, whereas the original substance did not do so.

**OXALATES** ( $-\text{C}_2\text{O}_4$ , or  $-\text{O}$ ).—Use  $\text{Am}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , (or  $\text{Am}_2\text{O} \cdot 2\text{H}_2\text{O}$ ).

**317.** Strong  $\text{H}_2\text{SO}_4$  heated with solid  $\text{Am}_2\text{O} \cdot 2\text{H}_2\text{O}$  causes an effervescence of gas consisting of a mixture of CO and  $\text{CO}_2$ :



The CO is detected by burning with a blue flame when a light is applied, the  $\text{CO}_2$  by rendering a drop of lime-water on a glass rod milky.

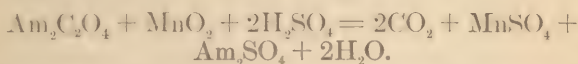
No blackening or charring is produced by strong  $\text{H}_2\text{SO}_4$ ; oxalates differ in this respect from the salts of all other organic acids.

**318.**  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ , or lime-water, added to  $\text{Am}_2\text{C}_2\text{O}_4$  solution (made by diluting some of the reagent solution in a test-tube with an equal quantity of water), gives a white precipitate ( $\text{CaC}_2\text{O}_4$ ), insoluble in  $\text{AmHIO}$  and in  $\text{H}\bar{\text{A}}$ , soluble in  $\text{HCl}$  or  $\text{HNO}_3$ .

**318 a.** If this precipitate is filtered off, a portion placed on a watch-glass will not effervesce with dilute HCl; but if the remainder is dried and heated to dull redness on platinum foil, it is converted without blackening into  $\text{CaCO}_3$ , which effervesces with dilute HCl.

This is a general test for oxalate of K, Na, Ba, Sr, or Ca; oxalates of these metals leave *carbonates* on ignition which effervesce with an acid.

**319.** Heated with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$ , solid oxalates give off  $\text{CO}_2$ :



Since commercial  $\text{MnO}_2$  usually contains some carbonate, it will give off  $\text{CO}_2$  when treated with  $\text{H}_2\text{SO}_4$ . If the  $\text{MnO}_2$  to be used is not known to be free from carbonate the best way to make the test is to add to some of the  $\text{MnO}_2$  in a test-tube a little  $\text{H}_2\text{SO}_4$ , and heat to boiling; if  $\text{CO}_2$  is found in the tube by a glass rod with a drop of lime-water on its end, continue to boil, occasionally drawing fresh air into the test-tube by pushing down a glass tube near to the surface of the liquid and sucking out the air; as soon as no  $\text{CO}_2$  is detectable in the tube after boiling for a short time, and the liquid is distinctly acid, the  $\text{Am}_2\text{C}_2\text{O}_4$  is added and the mixture again heated,  $\text{CO}_2$  will be rapidly given off, and may be detected by the ordinary methods.

If the  $\text{MnO}_2$  gives no  $\text{CO}_2$  with  $\text{H}_2\text{SO}_4$ , proceed at once to add the  $\text{Am}_2\text{C}_2\text{O}_4$ , heat and test for  $\text{CO}_2$ .

*Hydrogen oxalate*, or *oxalic acid* ( $\text{H}_2\text{C}_2\text{O}_4$ , or  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  if crystallized), when heated in a glass tube closed at one end partly sublimes unaltered, and is partly decomposed, yielding vapors which cause coughing; it yields reactions (317) and (319). It dissolves in water to an acid, poisonous liquid.

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TARTRATES { For a neutral tartrate use  $\text{Na}_2\text{T} \cdot 2\text{H}_2\text{O}$   
 (—''C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, or { or KNaT; for an acid tartrate use  
 —''T). {  $\text{H}_2\text{T}$  or  $\text{NaHT}$ .

**320.** A solid tartrate or solid  $\text{H}_2\text{T}$ , when heated strongly in a tube, chars, giving off a smell of burnt sugar.

**321.** A solid tartrate or solid  $\text{H}_2\text{T}$  heated with strong  $\text{H}_2\text{SO}_4$  blackens, giving off a mixture of  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{SO}_2$ .

**322.**  $\text{AgNO}_3$  gives with solution of a neutral tartrate a white curdy precipitate ( $\text{Ag}_2\text{T}$ ), soluble in  $\text{AmHIO}$  and in  $\text{HNO}_3$ . Allow some of the above precipitate ( $\text{Ag}_2\text{T}$ ) to settle in a test-tube, and pour off as much of the liquid from above it as possible; then pour very dilute  $\text{AmHIO}$  drop by drop into the tube, until the precipitate, after being shaken up with the liquid, is nearly but *not quite* dissolved; then heat the test-tube gradually and gently by immersing it in a beaker of cold water and slowly raising its temperature to  $60^\circ$ , a brilliant mirror of  $\text{Ag}$  will form on the interior of the tube. If the liquid, instead of being slowly heated to  $60^\circ$ , be quickly boiled, the  $\text{Ag}$  deposits as a black precipitate, which is not so characteristic.

**323.**  $\text{CaCl}_2$  precipitates from a neutral tartrate solution white or crystalline  $\text{CaT}$ : the precipitate often separates only after shaking the liquid well and letting it stand for a time; it is soluble in acids and its formation is retarded by  $\text{AmCl}$  and other  $\text{Am}$ -salts. This precipitate is soluble in strong cold  $\text{KHO}$ ,<sup>1</sup> is reprecipitated by boiling, but dissolves again more or less completely on cooling.

Decant the liquid from the precipitate and pour upon the precipitate a little very dilute  $\text{AmHIO}$  in a test-tube, drop in a small crystal of  $\text{AgNO}_3$  and warm carefully as in (322). A silver mirror forms on the part of the glass on which the  $\text{AgNO}_3$  rests.

**324.**  $\text{KCl}$ , or better  $\text{KA}$ , if added to solution of  $\text{H}_2\text{T}$  or an acid tartrate, gives on stirring or shaking a white crystalline precipitate ( $\text{KHT}$ ). If  $\text{HA}$  is added at the same time, the precipitate may also be obtained with neutral tartrates. Addition of alcohol assists the formation of the precipitate, which is soluble in alkalies and in mineral acids.

<sup>1</sup> A milkiness remains, however, if the potash solution contains carbonate.

325. If a few drops of  $\text{Fe}_2\text{Cl}_6$  solution be added to  $\text{H}_2\text{T}$  or  $\text{KNaT}$  solution, then  $\text{KHO}$  or  $\text{AmHO}$  until the liquid is strongly alkaline, no precipitate forms. The precipitation of several other metals (*e. g.*,  $\text{Al}$ ,  $\text{Mn}$ ,  $\text{Cu}$ ) by alkalis is similarly prevented by  $\text{H}_2\text{T}$ : this is owing to the formation of a double tartrate of the alkali and the other metal, which salt is not decomposed by an alkali.

*Hydrogen tartrate*, or *tartaric acid* ( $\text{H}_2\text{T}$ ), occurs in colorless crystals which do not alter in the air; they taste pleasantly acid, and dissolve in water and in alcohol: they are detected by heating them alone or with strong  $\text{H}_2\text{SO}_4$  (320, 321): if dissolved and neutralized they also yield the reactions in (322, 323).

ACETATES. ( $-\text{C}_2\text{H}_3\text{O}_2$ , or  $-\text{A}$ ).—Use  $\text{NaA} \cdot 3\text{H}_2\text{O}$ .<sup>1</sup>

326. Solid  $\text{NaA}$  if strongly heated blackens, giving off a peculiar smell and a vapor (acetone) which burns with a bright flame when kindled.

327. Heated with strong  $\text{H}_2\text{SO}_4$ , vapor of  $\text{HA}$  is given off, recognized by its pungent smell of vinegar. If alcohol is first added to the  $\text{NaA}$  then strong  $\text{H}_2\text{SO}_4$ , and the mixture is warmed, a fragrant smell of ethyl-acetate ( $\text{EtA}$ ) is emitted; it is most decided when the liquid is shaken after cooling for a short time.

328.  $\text{Fe}_2\text{Cl}_6$  added in small quantity to a little  $\text{NaA}$  dissolved in water, gives a deep-red color: on boiling the solution, made neutral but not alkaline with  $\text{AmHO}$  (if necessary), all the  $\text{Fe}$  separates as a light-brown precipitate and the liquid becomes colorless. The red color of the solution before being boiled is changed to yellow by addition of  $\text{HCl}$  (difference from the coloration due to sulphocyanide).

*Hydrogen acetate*, or *acetic acid* ( $\text{HA}$ ).—"Glacial acetic acid" is at  $17^\circ \text{C}$ . a colorless crystalline substance, emitting when heated a very pungent and inflammable vapor: it is strongly acid. It dissolves in water readily, impart-

ing its peculiar smell to the liquid in a mild degree. The acid is completely volatile without decomposition.

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**329.** The above organic acid-radicles may be specially tested for by any of their reactions; (318) being generally used to test for an oxalate in solution, (317) or (319) when it is solid; a tartrate is best detected in solution by reaction (322) or (323), or if solid by (320); an acetate is found by (326) or (327).

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\* \* After completing the reactions for the acid-radicles the student may proceed to Section VI, unless he is intending to learn the analysis of simple salts, when he proceeds to Section V.



## SECTION V.

### ANALYSIS OF SIMPLE SUBSTANCES CONTAINING ONE METAL AND ONE ACID-RADICLE.<sup>1</sup>

*Note.*—This section may be neglected by a student who is proceeding through the senior analytical course.

330. The ordinary method of proceeding to detect the metal or acid-radicle or both in a simple substance, is to make a few preliminary experiments, which will usually give some idea as to what substance is present, and will occasionally even detect metal or acid-radicle, or both of them, with certainty. Whether the composition of the substance has been satisfactorily proved by this preliminary examination or not, the next process is to endeavor to dissolve the substance, if it is not already in the liquid form, in water or acids; then by adding to the solution certain group-reagents in the proper order of succession, it is found to which analytical group the metal present belongs. The following table gives the analytical groups for metals, each group being headed by its distinctive number, name, and group-reagent:

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<sup>1</sup> Two metals may occasionally be present, as when an alum, or tartar-emetic [ $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ ], is given for analysis; also there may be two acid-radicles in the liquid given for analysis, since a salt insoluble in water is occasionally dissolved in an acid; but the student should always be informed of this if it in any way complicates the analysis. It will not usually do so, since in the most commonly occurring case, that of an alkaline earth phosphate dissolved in  $HCl$ , the  $PO_4$  is detected in Group III, and accordingly no other acid-radicle is looked for.

Table showing the Analytical

<p><i>Note.</i>—It will be observed that there are two divisions of Groups II and III. In analysis it is usual to separate the two divisions of Group II from one another, after having separated the whole group from the remaining groups; the two divisions of Group III are by some analysts precipitated together and subsequently separated; they are, however, often precipitated separately, and treated as distinct groups.</p>	<p>Metals whose chlorides are insoluble in water and dilute acids, and which are therefore precipitated from their solutions by hydrochloric acid.</p>	<p>Metals whose sulphides are insoluble in dilute acids, and which are therefore precipitated from acid solutions of sulphuretted hydrogen.</p>	
	<p>GROUP I. <i>Hydrochloric Acid, or Silver Group.</i></p>	<p>GROUP II. <i>Sulphuretted Hydrogen Group.</i></p>	
		<p>{ GROUP II A. { <i>Copper Group.</i> Sulphides insoluble in NaHO and in <math>\text{Am}_2\text{S}</math>.</p>	<p>{ Group II B. { <i>Arsenic Group.</i> Sulphides soluble in NaHO and in <math>\text{Am}_2\text{S}</math>.</p>
	<p>Lead, . . . . Pb Silver, . . . . Ag Mercurous, . . . Hg'</p> <p>1</p>	<p>Mercuric, <math>\text{Hg}''</math> [Lead, . . . . Pb] Bismuth, . . . Bi Copper, . . . . Cu Cadmium, . . . Cd</p> <p>2</p>	<p>Tin, . . . . Arsenic, . . . Antimony, . .</p> <p>3</p>

After discovering to which of the above analytical groups the metal present belongs, it is identified by the properties or appearance of the group-precipitate, and its presence confirmed, if necessary, by special tests made on the precipitate or on another portion of the "original solution."<sup>1</sup>

The acid-radicle, if it has not been already detected during the examination for the metal, is tested for in a less systematic manner. A few preliminary experiments are first performed, and if these do not detect the acid-radicle, it is found, partly by a systematic examination, including that described above for the detection of the metal, but more commonly by special tests.

A substance insoluble in water and in acids is examined according to the special directions in (367-369).

Since in these analyses only one metal and one acid-radicle are to be looked for, the examination for the metal is carried no further when one metal has been detected with certainty, and the examination for the acid-radicle

<sup>1</sup> By the "original solution" is meant the solution of the substance, or the substance itself, if a liquid is under analysis, to which no reagent has been added.

*Classification of the Metals.*

Metals which are precipitated as hydrates from their solutions containing ammonium chloride when made alkaline with ammonia, or as sulphides or hydrates when ammonium sulphide or sulphuretted hydrogen is subsequently added.		Metals whose carbonates are precipitated by addition of ammonium carbonate in the presence of ammonium chloride.	Metals whose solutions are not precipitated by any of the foregoing group-reagents in the presence of ammonium chloride.
GROUP III. <i>Ammonia and Ammonium-sulphide Group.</i>		GROUP IV. <i>Ammonium-carbonate or Barium Group.</i>	GROUP V. <i>Potassium Group.</i>
GROUP III A. <i>Alumina or Iron Group.</i>	GROUP III B. { <i>Ammonium sulphide or Zinc Group.</i>		
Aluminium, . . Al Iron, . . . Fe Chromium, . . Cr	Zinc, . . . Zn Manganese, . Mn Nickel, . . . Ni Cobalt, . . . Co	Barium, . . . Ba Strontium, . . Sr Calcium, . . . Ca	Ammonium, . . NH <sub>4</sub> Potassium, . . K Sodium, . . . Na Magnesium, . . Mg
4	5	6	7

is similarly at an end when the presence of one such radicle has been satisfactorily proved. It must, however, be understood that substances given for analysis are liable to contain impurities, which will yield only slight indications; if in the course of analysis, therefore, *only a slight* result is obtained, proceed until some substance is detected in larger quantity, entering against the slight result "Trace of —."

The separation and washing of a precipitate by "decantation" (23 *b*, 24 *b*) is recommended wherever it is possible, as this process is more easily performed than that of filtration (23 *a*); if a precipitate, however, refuses to settle after heating and shaking the liquid, filtration must usually be resorted to.

*Caution.*—In every analysis each result must be fully entered in the note-book *as soon as the experiment has been performed*, the form of entry being the same as that adopted for the directions in the text.

For examples of substances to be given for analysis by Section V, see par. 537.

\* \* \* The numbers in brackets refer to the paragraphs in the text, in which tests or processes to be employed by the student are fully described.

## DIRECTIONS FOR THE ANALYSIS OF A SIMPLE SUBSTANCE.

The substance given for analysis may be either a solid or a liquid. If it is a solid examine by (331 *et seq.*) omitting (334), if a liquid is to be analyzed begin at (334).

### THE SUBSTANCE GIVEN FOR ANALYSIS IS A SOLID.

**331.** Make a careful examination of the properties of the substance, noting down its color,<sup>1</sup> its smell, if it possesses any, also its form—whether it is in powder, crystals, or non-crystalline pieces; note carefully also any appearance or property which may strike you on examining the substance with the naked eye or with the assistance of a lens; after noting down the results of this examination, the substance is powdered as finely as possible.

If the substance possesses a metallic lustre or appearance, work as directed under (366); if it is not metallic in appearance, proceed to ascertain its solubility by the directions contained in (332), and, according to the result thus obtained, conduct the further analysis of the substance by (333) or by (367).

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<sup>1</sup> The salts of the following metals are colored: Cu, *blue*; Fe<sup>+++</sup>, *brownish-yellow*; Fe<sup>++</sup>, *pale green*; Ni, Cr, Cr<sub>2</sub>O<sub>3</sub>, *green*; Mn, *salmon-pink*; Co, *reddish-pink*. Chromates, *light yellow*; dichromates, *orange-red*; Sb<sub>2</sub>S<sub>3</sub>, CaO, MnO<sub>2</sub>, *black*; HgO, Pb<sub>3</sub>O<sub>4</sub>, *red*; PbO<sub>2</sub>, *dark brown*; PbO, *light brown*; Cr<sub>2</sub>O<sub>3</sub>, *green*.

## SOLUBILITY OF THE SUBSTANCE.

332. Since the method of examination of a solid substance depends upon whether it is soluble or insoluble in water or acids, the following experiments are tried.

Place a small quantity of the finely powdered substance in a broad test-tube or a boiling-tube, fill the tube about one-third with water, and heat to boiling:

<p><i>The substance dissolves.</i></p> <p>After examining a portion of the solid substance by the preliminary tests (333) and (335-338 a) proceed to examine the color and reaction of the liquid to litmus by (334, I, II), and, refer to (339) for directions for analysis.</p>	<p><i>The substance does not dissolve:</i> heat a fresh portion with dilute HCl to boiling; if it does not dissolve, decant and boil the residue with strong HCl:</p>
<p>2. <i>The substance dissolves.</i></p> <p><i>Absence of Group I., except possibly Pb.</i></p> <p>After examining a portion of the solid substance by the preliminary tests (333) and (335-338 a) proceed to examine the HCl solution (after noting its color, see 334, I) for the metal by (339).</p>	<p><i>The substance does not dissolve:</i> put aside the test-tube containing the substance with HCl, and stir a fresh portion of the substance with a little dilute <math>\text{HNO}_3</math>; if it is not dissolved, boil. If dilute <math>\text{HNO}_3</math> does not dissolve it, heat with a little strong <math>\text{HNO}_3</math>:</p> <p>3. <i>The substance dissolves.</i></p> <p>After examining a portion of the solid substance by the preliminary tests (333) and (335-338 a) examine the <math>\text{HNO}_3</math> solution (after noting its color, see 334, I) for the metal by (339), taking care after testing for Group I by HCl to boil down considerably in a porcelain dish after adding a little strong HCl,<sup>1</sup> and then add dilute HCl before testing for Group II by <math>\text{H}_2\text{S}</math>.</p>
	<p><i>The substance does not dissolve:</i> mix together the contents of the two tubes in which the substance was heated with HCl and with <math>\text{HNO}_3</math>, and heat the mixture:</p> <p>4. <i>The substance dissolves.</i></p> <p>After examining a portion of the solid substance by the preliminary tests (333) and (335-338 a) examine the solution in <math>\text{HNO}_3</math> and HCl mixed as directed in the preceding column (332, 3) for the metal by (359).</p> <p>5. <i>The substance does not dissolve.</i></p> <p>Examine a fresh portion of the substance by (367 et seq.).</p>

<sup>1</sup> This method of proceeding removes  $\text{HNO}_3$ , which would cause with  $\text{H}_2\text{S}$  a deposit of S.



## PRELIMINARY EXAMINATION OF A SOLUBLE SOLID.

**333.** The table is thus arranged: In the first column is placed the experiment to be made; in the second a list of the results, any one or more of which may be observed; and in the third the inferences to be drawn from the results. Confirmatory or supplementary experiments are occasionally entered; they are, however, only to be tried when the result preceding them in the second column has been noticed.

A more complete preliminary examination will be found in (387-408).

Experiment.	Observation.	Inferences.
I. Heat a portion of the substance in an ignition-tube, or in a small dry test-tube, first gently and at last to redness.	I. The substance does not change, . . .	Absence of volatile, fusible and organic substances, and of water.
	II. The substance changes:	
	1. Drops of water condense in the top of the tube.	Presence of $H_2O$ .
	2. The substance fuses easily, . . .	Probable presence of a salt of Na or K, or of Ba, Sr, Ca, Mg.
	3. The substance sublimes, . . .	Presence of a salt of $NH_4$ , As, or Hg; possibly also of $H_2C_2O_4$ , of S (yellow), and of I (purple vapor).
Confirmatory. — Boil another portion of the substance with $KHO$ solution.	A smell of $NH_3$ is evolved and white fumes appear when a rod moistened with strong $HCl$ is held to the mouth of the tube.	Presence of $NH_4$ . Confirm by $PtCl_4$ (52), and proceed to (335).
Confirmatory. — Mix another portion of the substance with about three times as much powdered $Na_2CO_3$ and $KCy$ and heat in an ignition-tube.	A gray sublimate of minute metallic globules, best seen by a lens.	Presence of Hg. Pour upon the original substance a few drops of $AmHO$ , if it blackens $Hg'$ is present, if not, $Hg''$ is present.
	A black mirror-like sublimate, . . .	Presence of As.
	4. The substance blackens, and gives off $CO_2$ , which makes a drop of lime-water on a glass rod milky.	Presence of an organic acid-radicle, probably A, O or T: the last is known by a smell of burnt sugar.
	If the cool residue in the tube effervesces with $HCl$ , whereas the original substance did not.	The organic acid-radicle is united with K, Na, Ba, Sr, Ca, or Mg.

Experiment.	Observation.	Inference.												
	<p>5. Gas or vapor is given off; smell the vapor: Red nitrous fumes recognized by their smell. <math>\text{SO}_2</math>, known by its smell and by turning <math>\text{K}_2\text{Cr}_2\text{O}_7</math> solution green.</p> <p>Cl, Br, I, known by smell and color: Br and I by action on starch-paste, and Cl by bleaching moist litmus. A slip of wood with a spark at its end glows brightly or bursts into flame.</p> <p>The gas can be lighted and burns at the mouth of the tube; note the color of the flame: <i>Pale greenish-yellow</i>: the gas burns explosively, and nitrous fumes are seen. <i>Bright white</i>, the unburnt gas smells of garlic. <i>Peachblossom-colored flame</i>, gray sublimate of Hg.</p> <p>6. The substance changes color:</p> <table><tr><td><i>Yellow,</i></td><td>hot.</td><td><i>White,</i></td><td>cold.</td></tr><tr><td><i>Yellow-brown,</i></td><td>"</td><td><i>Yellow,</i></td><td>"</td></tr><tr><td><i>Dark red or brown;</i></td><td>"</td><td><i>Red-brown,</i></td><td>"</td></tr></table>	<i>Yellow,</i>	hot.	<i>White,</i>	cold.	<i>Yellow-brown,</i>	"	<i>Yellow,</i>	"	<i>Dark red or brown;</i>	"	<i>Red-brown,</i>	"	<p>From nitrate of a heavy metal. From combustion of free S or a sulphide: possibly also from a sulphate, sulphite, or theiosulphate. From certain chlorides, bromides, or iodides, also free I. O from chlorate or nitrate, or <math>\text{N}_2\text{O}</math> from decomposition of <math>\text{NH}_4\text{NO}_3</math>.</p> <p>Presence of <math>\text{NH}_3</math>, from strongly heated <math>\text{NH}_4\text{NO}_3</math>. Presence of <math>\text{PH}_3</math>, probably from a hypophosphite. Presence of Cy, from <math>\text{HgCy}_2</math>.</p> <p><math>\text{ZnO}</math>. <math>\text{PbO}</math>, <math>\text{SnO}_2</math> or <math>\text{Bi}_2\text{O}_3</math>. <math>\text{Fe}_2\text{O}_3</math>.</p>
<i>Yellow,</i>	hot.	<i>White,</i>	cold.											
<i>Yellow-brown,</i>	"	<i>Yellow,</i>	"											
<i>Dark red or brown;</i>	"	<i>Red-brown,</i>	"											
II. Dip into the powdered substance a moistened loop of platinum wire, and hold the loop in the Bunsen flame; moisten with strong HCl, and again hold in the flame.	<p>1. The flame is not colored, . . . . .</p> <p>2. The flame is colored:</p> <p><i>Intense yellow</i>,<sup>1</sup> . . . . .</p> <p><i>Pale violet</i>,<sup>1</sup> appearing <i>crimson-red</i> through the indigo-prism, . . . . . }</p> <p><i>Red</i> { <i>Appearing green</i> through the indigo-prism, . . . . .           <i>Appearing intense red</i> through the indigo-prism, . . . . . }</p> <p><i>Green</i> { <i>Yellowish-green</i>, . . . . .           <i>Bright green</i> with <i>blue</i> centre after moistening with HCl, . . . . .           <i>Green</i>, . . . . . }</p> <p><i>Blue</i> { <i>Pale blue (livid)</i>, . . . . .           <i>Vivid blue</i>, . . . . . }</p>	<p>Probable absence of the substances enumerated below.</p> <p>Presence of Na.</p> <p>" K.</p> <p>" Ca.</p> <p>" Sr.</p> <p>" Ba.</p> <p>" Cu.</p> <p>" <math>\text{B}_2\text{O}_3</math>.</p> <p>Presence of As, Sb, Pb. " <math>\text{CuCl}_2</math>.</p>												

<sup>1</sup> If the coloration for Na or K is intense, no further examination for the metal is necessary, but the presence of K should be confirmed by stirring with  $\text{PtCl}_4$  (47). Proceed to §35. If the coloration is slight, a trace only of the metal is present, and the examination for another metal is continued.

Experiment.	Observation.	Inference.														
III. Heat a portion of the substance in a cavity scooped on charcoal, in the blowpipe flame. <i>Confirmatory.</i> — Detach a small portion of the white mass, place it on red litmus paper and moisten it with a drop of water. <i>Confirmatory.</i> — If the moist residue is not alkaline to test-paper, moisten the remainder on the charcoal with $\text{Co}(\text{NO}_3)_2$ solution and heat again strongly in the blowpipe flame.	1. The charcoal "deflagrates," or burns rapidly. 2. A white mass is left in the charcoal which does not fuse, and shines brightly when strongly heated. The red paper becomes blue in a short time where the substance rests.  A blue residue, . . . . .  A pink residue, . . . . .  A green residue, . . . . .  3. The residue is not white and does not consist of globules of metal, neither is there any incrustation formed upon the charcoal; proceed to Exp. IV. 4. The residue contains metallic globules or an incrustation forms on the charcoal: proceed to Exp. V, omitting Exp. IV.	Presence of a nitrate or chlorate. Presence of Ba, Sr, Ca, Mg, Al, or Zn.  Presence of Ba, Sr, Ca, or possibly of Mg.  Presence of Al, or possibly of a phosphate, silicate, or borate. Presence of Mg.  " Zn.														
IV. Fuse a small quantity <sup>1</sup> of the substance into a clear colorless borax bead, first in the inner, then in the outer flame, noting in both cases the color of the bead whilst hot and when cold.  <i>Confirmatory.</i> — The presence of Cr or Mn may be confirmed by fusing a portion of the substance on platinum foil or wire with $\text{Na}_2\text{CO}_3$ and $\text{KNO}_3$ .	The bead is colorless when heated in both flames.  The bead is colored: <table><tr><th>In outer flame.</th><th>In inner flame.</th></tr><tr><td>Blue, hot; green, cold.</td><td>Red or colorless.</td></tr><tr><td>Blue, hot and cold.</td><td>Blue, hot and cold.</td></tr><tr><td>Brown or dingy purple, hot; light brown, cold.</td><td>Gray or black, hot and cold.</td></tr><tr><td>Brown, hot; yellow, cold.</td><td>Bottle-green, hot and cold.</td></tr><tr><td>Green,<sup>2</sup> hot and cold.</td><td>Green, hot and cold.</td></tr><tr><td>Purple, hot and cold.</td><td>Colorless, hot and cold.</td></tr></table> A yellow mass on cooling, . . . . .  A bluish-green mass on cooling, . . . . .	In outer flame.	In inner flame.	Blue, hot; green, cold.	Red or colorless.	Blue, hot and cold.	Blue, hot and cold.	Brown or dingy purple, hot; light brown, cold.	Gray or black, hot and cold.	Brown, hot; yellow, cold.	Bottle-green, hot and cold.	Green, <sup>2</sup> hot and cold.	Green, hot and cold.	Purple, hot and cold.	Colorless, hot and cold.	Absence of the metals below.  Presence of Cu. " Co. " Ni. " Fe. <sup>3</sup> " Cr. " Mn.  " Cr. " Mn.
In outer flame.	In inner flame.															
Blue, hot; green, cold.	Red or colorless.															
Blue, hot and cold.	Blue, hot and cold.															
Brown or dingy purple, hot; light brown, cold.	Gray or black, hot and cold.															
Brown, hot; yellow, cold.	Bottle-green, hot and cold.															
Green, <sup>2</sup> hot and cold.	Green, hot and cold.															
Purple, hot and cold.	Colorless, hot and cold.															

<sup>1</sup> It is necessary to adjust carefully the quantity of substance fused into the bead: if too much is used, the bead will often appear opaque; if too little is employed, one of the metals may escape detection. It is best at first to fuse only a minute quantity into the bead, adding more if no color, or but a faint color, is produced.

<sup>2</sup> Cr if present as a chromate gives a bead brown whilst hot, after having being fused in the outer blowpipe flame; but this brown color is not reproduced in the case of Cr when the bead, after becoming green by being heated in the inner flame, is again heated in the outer flame.

Experiment.	Observation.		Inference.
V. Mix the substance in a small cavity on wood-charcoal with $\text{Na}_2\text{CO}_3$ and $\text{KCy}$ , and heat strongly in the inner blowpipe flame for several minutes.	Metallic scales or globules are obtained, or an incrustation on the charcoal:		
	<i>Globules.</i>	<i>Incrustation.</i>	
	White and brittle.	White, . . . . .	Presence of Sb.
	White and brittle.	Yellow, . . . . .	" Bi.
	Red and malleable.	None, . . . . .	" Cu.
	White and malleable, marking paper easily.	Yellow, . . . . .	" Pb.
If metallic globules are obtained, detach one and strike it sharply on the bottom of an inverted mortar with the pestle, and note whether it is crushed to powder ( <i>brittle</i> ) or merely flattened out into a cake ( <i>malleable</i> ).	White and malleable, not marking paper, and readily fusible.	None, . . . . .	" Sn.
	White and malleable, not marking paper, fusible only with difficulty.	None, . . . . .	" Ag.
	None, . . . . .	{ Yellow whilst hot, white when cold; becomes green when moistened with $\text{Co}(\text{NO}_3)_2$ solution and reheated in the outer flame. }	" Zn.
If the globules are white and malleable, take one upon the point of a pen-knife and see if it will mark paper as a black lead-pencil does.	None, . . . . .	Brown, . . . . .	" Cd.
	None, . . . . .	White; on smelling the charcoal a smell of onions is perceived.	" As.

After the completion of the preliminary tests for the metal, a solution of the substance is made according to the directions in (332), and this solution is examined as there directed.

## 334. PRELIMINARY EXAMINATION OF A LIQUID.

Experiment.	Observation.	Inference.
I. Note the color of the liquid.  <i>Note.</i> —If the color has to be observed by night it should be examined by the white light obtained by burning a piece of magnesium ribbon. Delicate tints are best seen by looking through some thickness of the liquid at a sheet of perfectly white paper.	<i>Pink.</i> { Very delicate, . . . . . Intense, . . . . . Very delicate, . . . . .	Presence of Mn or dilute Co solution. Presence of Co. " Fe", or Ni or Cr in dilute solution.
	<i>Green.</i> { Intense, . . . . . Reddish-yellow, . . . . .	" Ni, Cr, or Cu. " Fe" or a bi-chromate.
	<i>Yellow.</i> { Light yellow, . . . . .	" neutral chromate.
	<i>Blue,</i> . . . . . <i>Violet or purple,</i> . . . . .	" Cu. " Cr or a permanganate.
	The liquid is colorless, . . . . .	Absence of Co, Ni, Cr, Cu, etc.
	<i>It is neutral,</i> . . . . . (Not affecting the color of either paper.)	Absence of free acids and alkalis, and of all salts but some of those of Am, Na, K, Mg, Ba, Sr, Ca, Ag.
	<i>It is acid,</i> . . . . . (Turning blue paper red.) If, on adding $\text{Na}_2\text{CO}_3$ to a part of the solution and warming, no effervescence occurs, free acid and acid salt are absent.	Presence of a free acid, of an acid salt, or of a salt with acid reaction.
II. Dip pieces of red and blue litmus-paper into the liquid.	<i>It is alkaline,</i> . . . . . (Turning red paper blue.) If the color of the paper becomes only slightly changed it indicates, probably, the presence of an alkaline salt.	Presence of a hydrate of K, Na, Am, Ca, Sr, or Ba, or of a salt with alkaline reaction.



Experiment.	Observation.	Inference.
III. Evaporate (21) some of the liquid upon a thin watch glass <sup>1</sup> heated very gently by supporting it some inches above a small flame upon a piece of wire gauze, or by means of a sand or water bath. If a residue remains on the glass bring this gradually into the flame and heat it more strongly.	<i>A residue is left,</i> . . . . . On being strongly heated the residue blackens and emits a smell of burning, : The smell resembles that of burning sugar.  <i>Note.</i> —If the cold residue after ignition effervesces with a drop of HCl, whereas the unignited residue did not, the organic acid-radicle is united with Ba, Sr, Ca, Mg, Na, or K. The results in Exp. I, par. 333, may be here observed and should be noted. Keep this residue for Exp. VI.	Presence of some dissolved solid. Pres. of $\overline{A}$ , $\overline{O}$ , or $\overline{T}$ . Pres. of $\overline{T}$ .
	<i>No residue is left,</i> . . . . . If the liquid is also colorless, tasteless, and without action on litmus-paper, it must consist only of distilled water, and no further examination of it need be made. If the liquid is alkaline, $\text{NH}_3$ must be looked for; if it is acid, $\text{H}_2\text{CO}_3$ , $\text{H}_2\text{SO}_3$ , $\text{HCl}$ , $\text{HNO}_3$ , $\text{H}_2\text{SO}_4$ , and other volatile acids only need be tested for.	Absence of any dissolved solid.
IV. Add excess of strong NaHO or KHO solution and boil (51).	A smell of $\text{NH}_3$ ; moist red litmus is turned blue, and a rod moistened with strong HCl produces white fumes when held in the mouth of the test-tube.	Presence of $\text{NH}_4$ . No further test need be tried for a metal. Proceed to (335).
V. Experiment II (page 193) is then tried by dipping the platinum wire into the liquid, concentrated, if necessary, by evaporation.		
VI. Experiment IV (page 194) is tried by fusing some of the residue from Exp. III (above) in the borax bead.		

<sup>1</sup> A piece of thin glass from the side of a broken flask is a cheap and useful substitute for a watch-glass.

## PRELIMINARY EXAMINA-

335. Pour dilute  $\text{H}_2\text{SO}_4$  in excess upon the substance in a test-

336. A gas is evolved, shown by effervescence or by a charac-

1. Colorless gas without smell. A drop of lime or baryta water, held in the tube upon the end of a glass rod becomes milky: <i>Presence of a carbonate.</i>	2. Gas smelling of sulphur. A drop of $\text{K}_2\text{Cr}_2\text{O}_7$ solution held in the tube upon the end of a glass rod, becomes green: <i>Presence of a sulphide.</i>	3. Gas with a most fetid smell. A slip of filter-paper moistened with alkaline solution of $\text{PbA}_2$ and held in the tube, is blackened: <i>Presence of a sulphide.</i>	4. Yellow gas smelling of $\text{Cl}$ . A slip of moist litmus-paper held in the tube is bleached: <i>Presence of a hypochlorite.</i>
	2a. The $\text{SO}_2$ gas is given off only after standing for a time or on warming, and yellow S separates: <i>Presence of a theiosulphate.</i>		

337. Add strong  $\text{H}_2\text{SO}_4$  in small quantity to a fresh portion of any of the results enumerated below occurs;<sup>1</sup> if none of them is

1. Fumes are evolved with pungent smell and acid reaction to litmus-paper, the liquid is not colored: <i>Presence of a chloride or nitrate.</i>	2. The liquid becomes yellow or red, and a chlorous smell is given off; on warming the tube a crackling noise or slight explosion is produced: <i>Presence of a chlorate.</i>
Confirmatory.—Hold in the fumes a glass rod moistened with a solution of $\text{AgNO}_3$ acidified with $\text{HNO}_3$ ; the solution on the rod becomes milky: <i>Presence of a chloride.</i>  Confirm by (351).	Confirmatory.—Drop into the acid some small pieces of Cu; reddish-brown gas is evolved: <i>Presence of a nitrate.</i>  Confirmatory.—To a portion of the cold solution of the substance in water add a few drops of dilute indigo solution, then some $\text{H}_2\text{SO}_4$ ; the blue color of the indigo is destroyed.

338. After heating the tube containing the strong  $\text{H}_2\text{SO}_4$  and porcelain dish for (338 a); rinse out the tube, and dry the inside of a fluoride is shown. The presence of a fluoride, if decisively

338a. Add to the liquid in the porcelain dish alcohol, mix by a greenish tinge it shows: *Presence of a borate* (confirm by 353).

<sup>1</sup> If Pb, Ba, Sr, or Ca is present the addition of  $\text{H}_2\text{SO}_4$  causes a

## TION FOR THE ACID-RADICLE.

tube, and observe the effect produced;<sup>1</sup> then heat to boiling: teristic smell; see below:

<p>5. <i>Reddish-brown fumes are evolved</i>, best seen by looking down the tube at white paper. On adding a little cold dilute <math>H_2SO_4</math> and <math>FeSO_4</math> solution to a fresh portion, a deep-brown liquid: <i>Presence of a nitrite.</i></p>	<p>6. <i>Smell of HCy.</i> Test for a cyanide and a ferro-, ferri-, and sulpho- cyanide in the original hypochlorite, nitrite substance by (351).</p> <p>7. <i>Smell of vinegar.</i> Refer to (337, 4) below.</p>	<p><i>No gas is evolved:</i> Absence of carbonate sulphite, theiosulphate, sulphide, substance by (351).  Pass on to (337).</p>
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the substance, mix well by shaking, heat the liquid and note whether noticed proceed to (338) and (338 a):

<p>3. <i>A reddish-brown or violet color</i> is produced in the acid, and no explosion or crackling occurs on warming: <i>Presence of a bromide or iodide.</i></p> <p>If on heating the mixture, colored vapor is evolved (see note), hold in the vapor the end of a glass rod covered with moist starch powder; the starch becomes brown: <i>Presence of a bromide.</i></p> <p>The starch becomes bluish-black: <i>Presence of an iodide.</i></p> <p><i>Note.</i>—The vapor is much more easily obtained by mixing the substance with <math>MnO_2</math> powder, before adding <math>H_2SO_4</math> and heating.</p>	<p>4. <i>A smell of vinegar</i> is noticed: <i>Presence of an acetate.</i></p> <p><i>Confirmatory.</i>—Add to a fresh portion of the substance some alcohol, then strong <math>H_2SO_4</math>; a fragrant smell proves an acetate.</p>	<p>5. <i>A mixture of CO and CO<sub>2</sub> gases</i> is given off: found by a drop of lime-water held in the tube being turned milky, and by the CO burning with a blue flame when kindled: <i>Presence of an oxalate.</i></p>	<p>6. <i>The substance blackens</i> and evolves gases, amongst which <math>SO_2</math> is recognized by its smell and its action on <math>K_2Cr_2O_7</math> solution: <i>Prob. presence of a tartrate.</i></p> <p>Confirm by (354).</p>
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substance, let it stand for some time, then pour the liquid into a thoroughly; if it is seen to be corroded and dimmed: *Presence* indicated here, requires no confirmation.

stirring, heat the dish and kindle the alcohol; if the flame has

precipitate of the insoluble sulphate; this may be disregarded.

## 339. GENERAL TABLE FOR THE

If the metal has not been detected in the preliminary experiment group it belongs (see table, pp. 188, 189), and then trying

A part of the solution of the substance, if acid (340), is mixed with dilute HCl (341):		
The precipitate may be: AgCl—white. Hg <sub>2</sub> Cl <sub>2</sub> — " PbCl <sub>2</sub> — "  Examine for the metal by Table I (344).	Into the same part of the solution (342) H <sub>2</sub> S is passed, or H <sub>2</sub> S is heated to boiling:	
	<p>The precipitate may be:</p> <p>HgS—black. PbS— " Bi<sub>2</sub>S<sub>3</sub>— " CuS— " CdS—yellow.</p> <p>SnS—brown. SnS<sub>2</sub>—yellow. Sb<sub>2</sub>S<sub>3</sub>—orange. As<sub>2</sub>S<sub>3</sub>—yellow.</p> <p>Examine for the metal by Table II (345).</p>	<p>To a fresh portion of the solution [Caution. — If a tartrate or evaporating the liquid must dilute HCl, and tested by If AmCl and AmHO produce and warmed. Should a (343) or fluoride (338) have</p> <p>The precipitate may be:</p> <p>Al<sub>2</sub>HO<sub>3</sub>—{ colorless and transparent. Cr<sub>2</sub>HO<sub>3</sub>—pale green. Fe<sub>2</sub>HO<sub>3</sub>—reddish-brown. FeHO<sub>2</sub>—{ dingy green turning brown in the air.</p> <p>Examine for the metal by Table III A (346).</p> <p>If the precipitate is opaque or white and has none of the above appearances refer to (357).</p>

If no metal can be found, the substance is probably an acid (see 334, II).

## NOTES TO THE GENERAL TABLE.

**340.** If the liquid is *neutral* or *alkaline*, a portion of it is made just acid by slowly dropping in dilute HNO<sub>3</sub>; if this produces no precipitate, or a precipitate which dissolves on adding more HNO<sub>3</sub>, another portion of the liquid is examined by the above table.

If a precipitate forms which is not dissolved by adding more HNO<sub>3</sub>, it may consist of colorless, gelatinous H<sub>4</sub>SiO<sub>4</sub> from a silicate, or finely divided S, which is precipitated *white* from a polysulphide, and *yellow* from a theiosulphate; or of SnO<sub>2</sub>, or metastannic acid, or Sb<sub>2</sub>O<sub>3</sub>, all white; it may also possibly be SnS<sub>2</sub>, As<sub>2</sub>S<sub>3</sub> (both yellow), Sb<sub>2</sub>S<sub>3</sub> (orange-red), these sulphides being precipitated from a sulphostannate, sulpharsenite, or sulphantimonite.

If H<sub>4</sub>SiO<sub>4</sub> separates, it is best to evaporate the acidified solution quite to dryness, then heat the residue with dilute HCl; any insoluble

## EXAMINATION FOR THE METAL.

mination, it is most rapidly found by ascertaining to which special tests for each member of the group.

by precipitate forms, more  $\text{HCl}$  is added and the liquid heated:

water is added to it (343), the liquid is then diluted, and if no precipitate has formed it

on  $\text{AmCl}$  is added, then  $\text{AmHO}$  in excess:

calate has been found by (37), some of the solid substance or the residue obtained by strongly heated on a piece of porcelain, the residue on cooling is then dissolved in  $\text{AmCl}$  and excess of  $\text{AmHO}$ .

precipitate, a few drops of the original solution are added to some  $\text{AmHMoO}_4$  yellow precipitate form, indicating the presence of a *phosphate*, or should a *chromate* be found refer to (37) for the examination of the Group III A precipitate.

to the same portion add a few drops of  $\text{Am}_2\text{S}$  or  $\text{H}_2\text{S}$ -water:

*Note*—Before adding  $\text{Am}_2\text{S}$  the liquid may be *blue*, showing *presence of Ni*, or *violet* on dissolved  $\text{Cr}_2\text{H}_2\text{O}_5$ ; the latter must be precipitated by long boiling in a porcelain dish before adding  $\text{Am}_2\text{S}$ .]

The precipitate may be:	To the same portion add $\text{Am}_2\text{CO}_3$ :		
$\text{ZnS}$ —white.	The precipitate may be:	To the same portion add $\text{Na}_2\text{HPO}_4$ , warm gently and shake well;	
$\text{MnS}$ —pink.		A white crystalline precipitate proves <i>presence of Mg</i> .	The metal still present may be $\text{NH}_4$ , Na, K; it should have been detected already in the preliminary examination by Tests I or II (333).
$\text{NiS}$ —black.			
$\text{CoS}$ — “			
$\text{FeS}$ — “	$\text{BaCO}_3$ —white.		
	$\text{SrCO}_3$ — “		
	$\text{CaCO}_3$ — “		
Examine for the metal by Table III B (347).	Examine for the metal by Table IV (348).		

ble residue confirms the presence of a silicate, it is filtered off, and the filtrate tested for the metal by the above general table.

Any other substance insoluble in dilute  $\text{HNO}_3$  is filtered off, and may generally be known by its appearance: further,  $\text{SnO}_2$  becomes *yellow* and  $\text{Sb}_2\text{O}_3$  *orange* when moistened with  $\text{H}_2\text{S}$ -water; metastannic acid becomes golden-yellow if moistened with  $\text{SnCl}_2$  solution.

**341.** Make a note of any changes which occur on the addition of  $\text{HCl}$ ; gases may be evolved (336), or a *yellow* solution may become *reddish-yellow*, which renders probable the presence of a neutral chromate.

**342.** Before  $\text{H}_2\text{S}$  is added, the liquid must be heated, and if any smell of  $\text{Cl}$  or of  $\text{SO}_2$  or brown nitrous fumes should be perceived, the solution must be boiled down nearly to dryness, then dilute  $\text{HCl}$  added and  $\text{H}_2\text{S}$  added at once. During evaporation gelatinous  $\text{H}_4\text{SiO}_4$  may separate (340).

**343.** The following changes occurring on the gradual addition of  $\text{H}_2\text{S}$  are of importance. If the precipitate is *white* at first, then *brown*, and at last *black*, the presence of  $\text{Hg}^{++}$  is shown; if the solution is



strongly acid and gives a *red* precipitate becoming *black* on dilution with  $H_2S$ -water  $Pb$  is present.

A separation of white  $S$  may occur accompanied by the following changes of color, which are characteristic and should be noted down:

A reddish-yellow solution changing to pale green indicates a ferric salt.				
A reddish-yellow	"	"	bright green	" chromate.
A green	"	"	colorless	" manganate.
A purple	"	"	colorless	" permanganate.

The precipitate of  $S$  is known by being perfectly white and running through a filter; it need not be further examined.

A yellow precipitate which forms only on boiling the liquid may be  $As_2S_3$  from an arsenate, or  $SnS_2$  from a stannic salt.

### 344. TABLE I.—SILVER GROUP.

A *white* precipitate forms on addition of  $HCl$ , and is either not dissolved when boiled with  $HCl$ , or it dissolves and reappears in crystals on cooling, the liquid showing the *presence of Pb*. The precipitate may consist of  $AgCl$ ,  $PbCl_2$ ,  $Hg_2Cl_2$ .

Let the precipitate settle and decant the liquid: boil the precipitate in the test-tube with  $AmHO$ :

1. The precipitate dissolves, at least in part (see note below):	2. The precipitate does not dissolve:	
<p>Presence of <i>Ag</i>.</p> <p>Confirm by adding excess of <math>HNO_3</math> to the <math>AmHO</math> solution; a milkiness appears.</p>	<p>The color of the precipitate is unchanged:</p> <p>Presence of <i>Pb</i>.</p>	<p>The precipitate becomes black:</p> <p>Presence of <i>Hg</i> (<i>Mercurous</i>).</p>
<p>Note.—Coagulated <math>AgCl</math> often dissolves only slowly in <math>AmHO</math>.</p>	<p>Confirm by decanting the liquid, dissolving the precipitate in <math>H\bar{A}</math>, and adding <math>K_2CrO_4</math> to the solution; a yellow precipitate forms.</p>	<p>Confirm by immersing a bright slip of copper in a portion of the original solution, made acid with a few drops of <math>HNO_3</math>; a gray deposit forms on the <math>Cu</math>, which becomes white and bright when rubbed.</p>

## 345. TABLE II.—COPPER AND ARSENIC GROUPS.

Note the color of the precipitate yielded by  $\text{H}_2\text{S}$ :

1. *The precipitate is dark brown or black*; it may consist of  $\text{SnS}$ ,  $\text{CuS}$ ,  $\text{HgS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{PbS}$ .

Add pure  $\text{NaHO}$  in excess to a small quantity of the liquid and precipitate, or of the precipitate alone after decanting the liquid if possible, and boil:

*The precipitate dissolves*: to a portion of the  $\text{NaHO}$  solution add  $\text{HCl}$  in excess; brown  $\text{SnS}$  is reprecipitated.

Boil another portion of the precipitate after adding a little yellow  $\text{As}_2\text{S}_3$ ; then add  $\text{HCl}$  in excess; a yellow precipitate of  $\text{SnS}_2$ :  
*Presence of  $\text{Sn}''$*   
(Stannosum).

The presence of  $\text{Sn}''$  should be confirmed by adding  $\text{HCl}$  to a part of the original  $\text{HCl}$  solution; a white precipitate shows *presence of  $\text{Sn}''$* .

*The precipitate does not dissolve*: it may consist of  $\text{CuS}$ ,  $\text{HgS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{PbS}$ .  
a. *The original solution is blue or green*, and becomes intensely blue on addition of excess of  $\text{AmHO}$ : *Presence of  $\text{Cu}$* . Confirm by adding a few drops of  $\text{H}_2\text{SO}_4$  to the original solution, and dipping into it a bright knife-blade or piece of steel; a red film of  $\text{Cu}$  deposits.

b. *The original solution is colorless*. Test in separate portions for  $\text{Hg}$ ,  $\text{Bi}$ ,  $\text{Pb}$  by the following special tests:

Immerse in the acid solution a bright strip of  $\text{Cu}$ ; a gray film is slowly deposited, which becomes brilliant white when rubbed:  
*Presence of  $\text{Hg}''$*   
Mercurium.

*Caution*. A salt of  $\text{Hg}''$  may have been converted into an  $\text{Hg}'$  salt during solution in  $\text{HNO}_3$ . The original substance should therefore be treated with  $\text{AmHO}$ ; if it blackens  $\text{Hg}'$  is present, if not  $\text{Hg}''$  was originally in the substance.

Pour another portion of the original solution into much cold distilled water; a white precipitate or milkiness:

*Presence of  $\text{Bi}$* .

*Note*.—If  $\text{Bi}$  is suspected and no milkiness appears, add excess of  $\text{AmHO}$  to the liquid;  $\text{Bi}$  if present acts as hydrate filter, pour one or two drops of boiling  $\text{HCl}$  upon the precipitate, and let them drop through into large excess of water; a milkiness on stirring shows *presence of  $\text{Bi}$* .

To a portion add  $\text{H}_2\text{SO}_4$ ; a white precipitate:

*Presence of  $\text{Pb}$* .

The presence of  $\text{Pb}$  should be confirmed by adding to a part of the original solution  $\text{AmHO}$  in excess, then  $\text{HAc}$  in excess, then  $\text{K}_2\text{CrO}_4$ ; a yellow precipitate shows *presence of  $\text{Pb}$* .

2. *The precipitate is yellow*: it may consist of  $\text{CdS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{SnS}_2$ .

Boil the precipitate with  $\text{NaHO}$  in excess, after decanting the liquid if possible:

*The precipitate does not dissolve*: it is bright yellow and pulverulent:

*Presence of  $\text{Cd}$* .

The presence of  $\text{Cd}$  may be confirmed by showing that the precipitate produced by  $\text{H}_2\text{S}$  dissolves on being boiled with dilute  $\text{H}_2\text{SO}_4$ .

*The precipitate dissolves*: it may consist of  $\text{As}_2\text{S}_3$  or  $\text{SnS}_2$ ; examine portions of the original solution as directed below:

Acidify a portion with  $\text{HCl}$ , and place in it a piece of  $\text{Zn}$  resting on a piece of platinum foil;  $\text{Sn}$  is deposited on the  $\text{Zn}$ :

*Presence of  $\text{Sn}''$*  (Stannicum).

The deposit of  $\text{Sn}$  should be detached from the  $\text{Zn}$ , and dissolved by boiling it in a test-tube with a little strong  $\text{HCl}$ ; then  $\text{HgCl}_2$  added; a white precipitate confirms the *presence of  $\text{Sn}''$* .

Acidify a portion with strong  $\text{HCl}$ , immerse in it some pieces of bright  $\text{Cu}$  and boil; a black film is deposited on the  $\text{Cu}$ :

*Presence of  $\text{As}$* .

*Note*.—If the yellow precipitate formed by  $\text{H}_2\text{S}$  appeared at once in the cold, the  $\text{As}$  is present as *Arsenosum*; if it formed only on boiling, *Arsenicum* is present.

3. *The precipitate is orange-red*: it may consist of  $\text{Sb}_2\text{S}_3$ .

Confirm by acidifying a portion of the original solution with  $\text{HCl}$  and immersing in it a piece of  $\text{Zn}$  resting on a slip of platinum foil; a black stain on the platinum (193):

*Presence of  $\text{Sb}$* .

*Note*.—It occasionally happens, if the solution has not been sufficiently diluted, that  $\text{H}_2\text{S}$  gives a reddish precipitate with  $\text{Pb}$  solution; such a precipitate, however, becomes black on adding more  $\text{H}_2\text{S}$ -water.

## 346. TABLE III A.—IRON GROUP.

The color of the precipitate produced by addition of  $\text{AmCl}$  and  $\text{AmHO}$  will usually indicate whether it contains  $\text{Fe}$ ,  $\text{Al}$ ,  $\text{Cr}$ ; the following tests may be made in confirmation.

To a portion of the original solution add  $\text{KHO}$  gradually until a precipitate has formed (see note below table), then add  $\text{KHO}$  in excess and stir well, one of the following results will be obtained:

1. A <i>colorless</i> gelatinous precipitate is produced, which dissolves in excess of $\text{KHO}$ to a <i>colorless</i> solution: the precipitate reappears on gradual addition of $\text{HCl}$ to the $\text{KHO}$ solution: <i>Presence of Al.</i>	2. A <i>pale-green</i> gelatinous precipitate forms, which dissolves in excess of $\text{KHO}$ to a <i>green</i> solution; when $\text{PbO}_2$ is added to this green solution and the liquid is boiled and then acidified with $\text{HA}$ , a yellow precipitate is produced: <i>Presence of Cr.</i>	3. A <i>reddish-brown</i> precipitate forms, insoluble in excess of $\text{KHO}$ . Add $\text{KCys}$ to the original $\text{HCl}$ solution, a blood-red coloration: <i>Presence of Fe<sup>III</sup>.</i>	4. A <i>dingy green</i> precipitate forms, insoluble in excess of $\text{KHO}$ ; the precipitate if filtered off and exposed to the air gradually becomes brown: <i>Presence of Fe<sup>II</sup>.</i>
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*Note.*—If a colorless gelatinous precipitate has been produced by  $\text{AmCl}$  and  $\text{AmHO}$ , and is not produced by addition of  $\text{KHO}$ , a silicate is probably present. Its presence is confirmed by fusing the solid substance in a bead of  $\text{NaAmHPO}_4$  (293); or by evaporating the acid solution to dryness, a residue insoluble in acid is  $\text{SiO}_2$ , and may be tested by the bead as directed above.

## 347. TABLE III B.—ZINC GROUP.

The color of the precipitate produced by addition of  $\text{Am}_2\text{S}$  or of  $\text{H}_2\text{S}$  to the alkaline solution will distinguish  $\text{Zn}$  or  $\text{Mn}$  from  $\text{Ni}$ ,  $\text{Co}$ , and  $\text{Fe}$ , and will usually distinguish  $\text{Zn}$  and  $\text{Mn}$  also from one another. See *a* and *b* below:

*a.* If the precipitate is light in color, add to some of the original solution  $\text{KHO}$  gradually until a precipitate forms, then add  $\text{KHO}$  in excess. A *white* precipitate, dissolving in excess of  $\text{KHO}$  and repre-

precipitated by addition of  $\text{H}_2\text{S}$  proves *presence of Zn*. A white or brownish precipitate, insoluble in excess of  $\text{KHO}$  and gradually turning dark brown when filtered off and exposed to the air shows *presence of Mn*.

*b.* If the precipitate is black it will consist of either  $\text{CoS}$  or  $\text{NiS}$  or possibly of  $\text{FeS}$ ; the distinction of the metals  $\text{Ni}$  and  $\text{Co}$  by the color of their solutions— $\text{Ni}$  being *green*,  $\text{Co}$  *pink*—and by the colors they impart to the borax bead is quite simple.  $\text{FeS}$  is only precipitated here from a *dilute* solution of a ferrous salt;  $\text{Fe}''$  is best detected by (346).

### 348. TABLE IV.—BARIUM GROUP.

Dip a loop of platinum wire into the original solution or into the  $\text{HCl}$  solution of the precipitate produced by  $\text{Am}_2\text{CO}_3$ , and hold the wire in the Bunsen flame. If the flame coloration thus obtained is not decisive, employ the tests placed at the foot of each column as confirmatory:

<p><i>A yellowish-green flame: Presence of Ba.</i></p> <p><i>Confirmatory.</i>—Add <math>\text{CaSO}_4</math> to a perfectly cold portion of the <math>\text{HCl}</math> solution; a precipitate forms <i>immediately</i>.</p> <p><i>Note.</i>—A brilliant green coloration may be produced by <math>\text{H}_3\text{BO}_3</math>.</p>	<p><i>A crimson flame, appearing deep red through the indigo-prism: Presence of Sr.</i></p> <p><i>Confirmatory.</i>—Add <math>\text{CaSO}_4</math> to a perfectly cold portion of the <math>\text{HCl}</math> solution; no precipitate is produced, but a precipitate appears <i>immediately</i> on boiling.</p>	<p><i>A red flame, appearing dingy-green through the indigo-prism: Presence of Ca.</i></p> <p><i>Confirmatory.</i>—Add <math>\text{CaSO}_4</math> to part of the <math>\text{HCl}</math> solution and boil; no precipitate. To the rest add <math>\text{AmHO}</math> in excess, and <math>\text{Am}_2\text{C}_2\text{O}_4</math>; a white precipitate forms.</p>
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### EXAMINATION FOR THE ACID-RADICLE.

349. If the acid-radicle has not been found already in the preliminary examinations (335–338 *a*), or during the examination for the metal (341, 343) or elsewhere, it must be tested for as directed below. Since the solubility of the substance (332) and the metal it contains are known, much trouble is usually saved by referring to the “Table of Solubilities” (455–458). Thus a salt of the metal found, which is insoluble in water, cannot be present if the substance is soluble in water or is a neutral liquid; and an insoluble salt cannot be present in an acid solution or in a substance which is soluble in acids.

For the tests given below, use separate portions of the original substance; try the tests in succession until an acid-radicle is found.

**350.** Acidify a portion of the liquid, or if a solid dissolve it, with dilute  $\text{HCl}$  and add  $\text{BaCl}_2$ . If  $\text{Pb}$ ,  $\text{Hg}'$ , or  $\text{Ag}$  has been found acidify with  $\text{HNO}_3$  and add  $\text{Ba}(\text{NO}_3)_2$ , since  $\text{HCl}$  and chlorides would precipitate the above metals as chlorides. A white precipitate forms which does not disappear on boiling: *Presence of a sulphate.*

**351.** Acidify a portion of the liquid, or if a solid is being examined dissolve the solid with dilute  $\text{HNO}_3$ ; filter off any precipitate or residue which may form, and add  $\text{AgNO}_3$  solution; a precipitate forms, which does not disappear on warming. Note the color of the precipitate; and according as it is white, yellow, or orange, examine it by 1, 2, or 3:

1. *The precipitate is white*; it may consist of  $\text{AgCl}$ ,  $\text{AgCy}$ ,  $\text{Ag}_4\text{FeCy}_3$ , or  $\text{AgCyS}$ . Make a portion of the original solution just acid with  $\text{HCl}$ , then add  $\text{Fe}_2\text{Cl}_6$ :

A deep-blue precipitate:  
*Presence of a ferrocyanide.*

A blood-red coloration:  
*Presence of a sulphocyanide.*

If  $\text{Fe}_2\text{Cl}_6$  has yielded neither a precipitate nor coloration, indicating absence of a ferro- and sulphocyanide, decant the liquid from the precipitate caused by  $\text{AgNO}_3$ , pour upon the precipitate some strong  $\text{HNO}_3$  and boil.

The precipitate remains undissolved:  
*Presence of a chloride.*

The precipitate dissolves:  
*Presence of a cyanide.*  
Confirm the presence of a cyanide in a portion of the original solution by boiling it with  $\text{FeSO}_4$ ,  $\text{Fe}_2\text{Cl}_6$ , and  $\text{KHO}$ , and acidifying with  $\text{HCl}$ ; a blue precipitate: *Presence of a cyanide.*

2. *The precipitate is yellow*, and may consist of  $\text{AgBr}$  or  $\text{AgI}$ .

Test some of the original solution for an iodide by adding to it starch solution and  $\text{KNO}_2$  solution, then acidifying (if not acid) with  $\text{HCl}$ ; a deep-blue coloration:

*Presence of an iodide.*

If an iodide is not thus detected, add to another portion of the original solution several drops of  $\text{Cl}$ -water; if the liquid becomes yellow, and on being shaken with  $\text{CS}_2$  colors that liquid reddish-brown, it shows:

*Presence of a bromide.*

3. *Orange-red precipitate.*

Make a portion of the original solution just acid with  $\text{HCl}$ , then add  $\text{FeSO}_4$  solution; a deep-blue precipitate shows:

*Presence of a ferrocyanide.*



*Note.*—If Hg has been found, HgCy<sub>2</sub> may be present, notwithstanding the formation of no precipitate with AgNO<sub>3</sub>. If not already detected in (333, I), refer to (306, *Note* 2, p. 180).

**352.** Acidify some of the original liquid, or if it is a solid dissolve it with dilute HNO<sub>3</sub>; filter if necessary, add a small quantity of this acid solution to some AmHMoO<sub>4</sub> solution, stir well and warm gently:

*A yellow precipitate shows:  
Presence of a phosphate.*

*If no precipitate forms heat to  
boiling; the formation of a yellow  
precipitate shows:*

*Presence of an arsenate.*

The presence of a phosphate or arsenate may be confirmed by dissolving the yellow precipitate, separated by filtration or decantation, by pouring upon it a little AmHO; on adding to this solution AmCl and MgSO<sub>4</sub>, a crystalline precipitate will form, which is to be filtered off and washed with a little cold water: several drops of AgNO<sub>3</sub> solution are poured upon this precipitate on the filter; if it becomes *yellow* a phosphate is present, if *brown* an arsenate is present. The presence of an arsenate is further confirmed by a yellow precipitate (As<sub>2</sub>S<sub>3</sub>) appearing with H<sub>2</sub>S when the liquor is boiled.

**353.** Acidify a portion of the original liquid, or if a solid stir it with HCl; dip into this solution a piece of turmeric-paper, and dry the paper at a gentle heat; if the paper becomes *reddish-brown* when dry, and changes to *dingy green* or *blue-black* when moistened with AmHO, the *presence of a borate* is shown.

**354.** The acid-radicles, *one* of which may still be present, are "T", "C<sub>2</sub>O<sub>4</sub>", and 'F. If the metal found belongs to Groups I, II, III, or IV, the examination for one of these radicles must be begun at (356); if the metal present is K, Na or NH<sub>4</sub> examine by (355).

**355.** Make the solution just alkaline with AmHO, then add CaCl<sub>2</sub> solution in some quantity, shake well and let stand if no precipitate forms at once: the preliminary examination (337) will usually have indicated which of these acid-radicles is present, and thus show

according to which of the three columns below the precipitate is to be further tested :

I. A crystalline precipitate appearing after some time, shows probable presence of a tartrate.

Confirm by 1 or 2 below :

1. Decant the liquid from the precipitate, add a little water and a single drop of  $\text{AmHO}$ , drop in a small crystal of  $\text{AgNO}_3$  and warm very carefully; a mirror is formed below the crystal, *presence of a tartrate*. This test may be tried also with the original solution by (322).
2. On acidifying some of the neutral original solution with  $\text{H}\bar{\text{A}}$  and adding alcohol and  $\text{KA}$  (unless  $\text{K}$  or  $\text{NH}_4$  has been detected in the substance), and stirring or shaking well, the formation of a crystalline precipitate shows *presence of a tartrate*.

II. A white pulverulent precipitate shows probable presence of an oxalate.

The presence of an oxalate, already indicated by the test in (337, 5), must be confirmed either by warming some of the original substance with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$ , and testing for  $\text{CO}_2$ -gas (319); or by the more tedious method of filtering off and drying some of the above precipitate of  $\text{CaC}_2\text{O}_4$ , then igniting it and testing for a carbonate with  $\text{HCl}$  (318 a).

III. A gelatinous flocculent precipitate shows probable presence of a fluoride.

Confirm by filtering and warming some of the precipitate, or of the substance if solid, in a small cup of lead or platinum with strong  $\text{H}_2\text{SO}_4$ ; fumes will be evolved which etch a properly prepared watch-glass (296).

**356.** An oxalate or fluoride of  $\text{Ba}$ ,  $\text{Sr}$ ,  $\text{Ca}$  or  $\text{Mg}$  will have been already detected. A tartrate of any one of these metals is found by gently heating the finely powdered substance if it is solid, or the neutral solution if a liquid, with *very dilute*  $\text{AmHO}$  and a crystal of  $\text{AgNO}_3$ : the formation of a mirror shows *presence of a tartrate*. If a metal of Groups I, II, or III has been found, the metal must be separated before testing for the acid-radicle.

If the metal belongs to Group I or II, make the original solution just acid with  $\text{HCl}$ , and add  $\text{H}_2\text{S}$  solution or pass  $\text{H}_2\text{S}$  (500 a) into the liquid for about five minutes; filter off the precipitate and add more  $\text{H}_2\text{S}$  to the filtrate; if no more precipitate forms,<sup>1</sup> boil in a porcelain dish until the liquid ceases to smell of  $\text{H}_2\text{S}$ , and examine by (355).

<sup>1</sup> If any further precipitate forms add more of the reagent, filter, and test again by adding more of the reagent; this addition of reagent, filtration, and testing the filtrate is repeated until no further precipitate forms on addition of the reagent to the filtrate.

If the metal belongs to Group III add  $\text{AmCl}$ ,  $\text{AmHIO}$  till alkaline, then  $\text{Am}_2\text{S}$ : boil and filter, add to the filtrate  $\text{Am}_2\text{S}$  if no more precipitate forms (see footnote, page 208), add  $\text{HIA}$  in excess, boil, filter off  $\text{S}$  if necessary, and examine by (355).

*Note.*—If no acid-radicle can be found in any quantity and the substance is not metallic in appearance, it is probably an oxide or a sulphide; most sulphides yield a sulphate or sulphuric acid when boiled with strong  $\text{HNO}_3$ , which may be detected after dilution by (350); an oxide may often be known by its color (see footnote, page 190) or by some other special property or test, *e. g.*,  $\text{MnO}_2$  by evolving  $\text{Cl}$  when heated with  $\text{HCl}$ ,  $\text{Pb}_3\text{O}_4$  by leaving brown  $\text{PbO}_2$  when treated with dilute  $\text{HNO}_3$ .

## EXAMINATION OF GROUP III A.

**357.** The precipitate formed by addition of  $\text{AmCl}$  and  $\text{AmHIO}$  to the solution of a substance insoluble in water may consist of  $\text{Al}_2\text{Ho}_6$ ,  $\text{Fe}_2\text{Ho}_6$ ,  $\text{Cr}_2\text{Ho}_6$ ; or of  $\text{Fe}$ ,  $\text{Al}$ ,  $\text{Cr}$ ,  $\text{Zn}$ ,  $\text{Mn}$ ,  $\text{Ni}$ ,  $\text{Co}$ ,  $\text{Ba}$ ,  $\text{Sr}$ ,  $\text{Ca}$ ,  $\text{Mg}$  as phosphate or oxalate; or of  $\text{Ba}$ ,  $\text{Sr}$ ,  $\text{Ca}$  as chromate or fluoride. The systematic examination of a precipitate in Group III A for these substances is a difficult matter; such an examination is, however, only necessary when an oxalate (337, 5), a chromate (343), or a fluoride (338) have been already detected, or when a phosphate is found. If a precipitate forms in Group III A, and the above acid-radicles are absent, proceed as directed in (346); if the above acid-radicles are present, the metal, unless certainly detected during the preliminary examination, must be tested for as directed below.

**358.** Note the appearance of the precipitate caused by  $\text{AmCl}$  and  $\text{AmHIO}$ , then add  $\text{Am}_2\text{S}$  to the liquid and precipitate, stir well, and note again the appearance of the precipitate: examine further by 1 or 2 (page 210).

1. *The precipitate after addition of  $\text{Am}_2\text{S}$  is black*; it may consist of  $\text{FeS}$ ,  $\text{CoS}$ , or  $\text{NiS}$ ; the means of distinguishing these three metals is given below. Note first the color of the original solution (334, 1).

<p><i>The color of the original solution was yellow or reddish-brown: Presence of <math>\text{Fe}^{+++}</math>. (Ferricum.)</i></p>	<p><i>b. The color of the original solution was pink, or possibly blue, becoming pink on dilution: Presence of Co.</i></p>	<p><i>c. The color of the original solution was green: Presence of Ni or <math>\text{Fe}^{++}</math>.</i></p> <p>Note the effect which was produced by the addition of <math>\text{AmCl}</math> and <math>\text{AmHO}</math>:</p>				
<p>This is confirmed by the precipitate produced by <math>\text{AmCl}</math> and <math>\text{AmHO}</math> in the original solution having been <i>pale-yellow or reddish-brown</i>, and becoming black on addition of <math>\text{Am}_2\text{S}</math>. As a confirmatory test add to a portion of the original solution, acidified with <math>\text{HCl}</math> if necessary, a few drops of <math>\text{KCys}</math> solution; a <i>blood-red</i> coloration is produced.</p>	<p>The presence of Co may be confirmed by adding excess of <math>\text{KHO}</math> to the original solution; a blue precipitate turning red on boiling shows the presence of Co.</p> <p>Co will also have been detected by its borax bead (333, IV).</p>	<table border="1"> <tr> <td data-bbox="583 553 792 844"> <p><i>A blue solution was produced: Presence of Ni.</i></p> <p>The presence of Ni may be confirmed by adding excess of <math>\text{KHO}</math> to a part of the original solution; a light-green precipitate shows the presence of Ni.</p> </td> <td data-bbox="792 553 985 844"> <p><i>A dingy-green precipitate, which, when shaken round in a porcelain dish and left for several minutes exposed to the air, becomes brown: Presence of <math>\text{Fe}^{++}</math>. (Ferrosium.)</i></p> </td> </tr> <tr> <td data-bbox="583 844 792 998"> <p>Ni will also have been detected by its borax bead (333, IV).</p> </td> <td data-bbox="792 844 985 998"> <p>Confirm by adding <math>\text{K}_2\text{Cfy}_2</math> to some of the original solution, acidified with <math>\text{HCl}</math> if necessary; a dark-blue precipitate is produced.</p> </td> </tr> </table>	<p><i>A blue solution was produced: Presence of Ni.</i></p> <p>The presence of Ni may be confirmed by adding excess of <math>\text{KHO}</math> to a part of the original solution; a light-green precipitate shows the presence of Ni.</p>	<p><i>A dingy-green precipitate, which, when shaken round in a porcelain dish and left for several minutes exposed to the air, becomes brown: Presence of <math>\text{Fe}^{++}</math>. (Ferrosium.)</i></p>	<p>Ni will also have been detected by its borax bead (333, IV).</p>	<p>Confirm by adding <math>\text{K}_2\text{Cfy}_2</math> to some of the original solution, acidified with <math>\text{HCl}</math> if necessary; a dark-blue precipitate is produced.</p>
<p><i>A blue solution was produced: Presence of Ni.</i></p> <p>The presence of Ni may be confirmed by adding excess of <math>\text{KHO}</math> to a part of the original solution; a light-green precipitate shows the presence of Ni.</p>	<p><i>A dingy-green precipitate, which, when shaken round in a porcelain dish and left for several minutes exposed to the air, becomes brown: Presence of <math>\text{Fe}^{++}</math>. (Ferrosium.)</i></p>					
<p>Ni will also have been detected by its borax bead (333, IV).</p>	<p>Confirm by adding <math>\text{K}_2\text{Cfy}_2</math> to some of the original solution, acidified with <math>\text{HCl}</math> if necessary; a dark-blue precipitate is produced.</p>					

2. *The precipitate, after addition of  $\text{Am}_2\text{S}$ , is white or light-colored.*—It may consist of  $\text{Cr}_2\text{HO}_6$ ,  $\text{Al}_2\text{HO}_6$ ,  $\text{ZnS}$ ,  $\text{MnS}$ ; [or of  $\text{BaCrO}_4$ , or Ba, Sr, Ca, Mg, as phosphate, oxalate, fluoride, silicate, or possibly borate.] The substances in brackets can, however, only be present if the liquid given for analysis was acid in reaction, or if a solid was given which was insoluble in water.

To a small portion of the original solution add  $\text{KHO}$  drop by drop until a precipitate is produced. (See note below the table.) Note the color and appearance of this precipitate, then add a larger quantity of  $\text{KHO}$  and stir or shake well; one of the following results (*a* or *b*) will be noticed:

a. The precipitate at first produced by  $KHO$  redissolves when the  $KHO$  is added in larger quantity; indicating the presence of  $Al$ ,  $Zn$ , or  $Cr$ . Note the appearance of the precipitate:

A pale-green flocculent precipitate:

Presence of  $Cr$ .

Confirm by boiling some of the green  $KHO$  solution with lead-peroxide ( $PbO_2$ ); a yellow liquid is obtained, which, if decanted, yields a yellow precipitate on addition of  $HA$  in excess.

The color of the solution and of the borax bead will also have detected  $Cr$ .

Note.—If the  $Cr$  was present as a chromate,  $AmCl$  and  $AmHO$  will have yielded no precipitate; but there will have been a green precipitate on addition of  $Am_2S$  and heating.

A white precipitate, which is reprecipitated from the  $KHO$  solution, by addition of a few drops of  $H_2S$ -water, but is not reprecipitated by addition of  $AmCl$ : Presence of  $Zn$ .

Confirmed by no precipitate having been produced by  $AmCl$  and  $AmHO$ , but a white precipitate by addition of  $Am_2S$ , or of  $H_2S$  after  $AmHO$ .

A white flocculent precipitate, not reprecipitated from the  $KHO$  solution by addition of a few drops of  $H_2S$ -water or by boiling, but reprecipitated immediately if sufficient  $AmCl$  solution is added:

Presence of  $Al$  (see note).

Note.— $AlPO_4$  is precipitated here also, and is soluble in  $KHO$ , but differs from  $Al_2H_6$  in being reprecipitated from the  $KHO$  solution by addition of excess of  $HA$ ; if  $PO_4$  has been detected the analysis is finished.  $AlPO_4$  is soluble only in acids, hence the original liquid must have been acid or the original solid substance insoluble in water.

Note.—Sometimes a flocculent precipitate is produced on adding  $AmCl$  and  $AmHO$  to the original solution, and yet no precipitate is produced by  $KHO$ ; this renders probable the presence of an alkaline silicate. In this case evaporate a portion of the solution to dryness with  $HCl$ ; warm the residue with  $HCl$ ; if any insoluble residue is left, the presence of a silicate is proved; filter and test the filtrate for  $K$  or  $Na$ .

b. The precipitate at first produced by  $KHO$  does not redissolve on addition of more  $KHO$ ; the precipitate will have one of the following appearances:

A white or dingy-yellow precipitate, rapidly darkening when shaken in the air:

Presence of  $Mn$ .

Confirmed in the preliminary examination by producing a green mass when fused with  $Na_2CO_3$  and  $KNO_3$ , and by no precipitate having been produced on addition of  $AmCl$  and  $AmHO$ , unless the solution was exposed for some time to the air.

A pale-yellow precipitate, not darkening in the air: this precipitate will also have been produced by  $AmCl$  and  $AmHO$  and its color will not have been altered by addition of  $Am_2S$ :

Presence of  $BaCrO_4$ .

$Ba$  has been already confirmed by the flame coloration (333, II), and a chromate by the change of color of the orange-red liquid to green on adding  $H_2S$  (343).

A white precipitate, not darkening in the air:

Presence of  $Ba$ ,  $Sr$ ,  $Ca$ , or  $Mg$  as phosphate, oxalate, etc.

Pass on to (359).

Note.—This precipitate can only be formed if the original solution was acid.



359. *The precipitate may consist of Ba, Sr, Ca, or Mg as phosphate, oxalate, borate,<sup>1</sup> fluoride, or silicate.*

Examine for the metal and acid-radicle as directed below, working through the columns from left to right, unless the presence of a phosphate (339), oxalate (333, I, 4, or 337, 5), borate (334, V, or 333, II, or 338 *a*), or fluoride (338) has been already proved, in which case proceed at once to examine according to (360), or by column 1, or 2, or 3 below.

If this precipitate is proved to contain a phosphate, oxalate, borate, fluoride, or silicate, the further examination for an acid-radicle becomes unnecessary.

1. Add AmHO in excess to a portion of the original solution, <sup>2</sup> filter, dry the precipitate and heat a portion of it to a dull red heat for several minutes on platinum foil. Place the foil in a test-tube and pour a few drops of dilute HCl upon it; if the residue dissolves with effervescence, it shows the presence of an oxalate. Test this HCl solution for Ba, Sr, Ca, Mg, by (339), using it as the original solution. If the ignited precipitate does not dissolve with effervescence, pass on to column 2.	2. Stir some of the precipitate produced by AmHO, <sup>2</sup> column 1, on a watch-glass, with a little water to which a few drops of HCl have been added, until the precipitate is dissolved. Dip into the liquid a slip of turmeric-paper, and dry at steam heat; the slip appears red-dish-brown, and becomes dingy green when moistened with AmHO: <i>Presence of a borate.</i> Examine for the metal present by (361). If a borate is not found, proceed to column 3.	3. Place another portion of the precipitate produced by AmHO, <sup>2</sup> column 1, in a leaden cup or platinum crucible, add strong H <sub>2</sub> SO <sub>4</sub> and warm gently, covering the vessel with a watch-glass, which has been coated with a film of wax and has had characters traced with a sharp point through the wax (296); the glass is etched: <i>Presence of a fluoride.</i> Examine for the metal present by (361). If no fluoride is found, proceed to column 4.	4. If phosphate, oxalate, borate and fluoride have been proved to be absent, a silicate is probably present. Test for it par. 361
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360. *Examination of a Phosphate—Explanation of Method.*—In order to detect Ba, Sr, Ca, or Mg present as phosphates the PO<sub>4</sub>

<sup>1</sup> Borates of Ba, Sr, and Ca, are rarely precipitated in Group III, since they are soluble in the AmCl formed on adding AmHO to the HCl solution.

<sup>2</sup> If a solid is being examined, a portion of the original solid is employed for this test, instead of the precipitate produced by AmHO in the HCl solution.

must be removed from the solution and the metal left as chloride. This is effected by neutralizing all HCl and leaving the solution acidified only by free HAc; by *gradual* addition of  $\text{Fe}_2\text{Cl}_6$  and boiling all  $\text{PO}_4$  is precipitated as  $\text{FePO}_4$  which, though soluble in HCl, is perfectly insoluble in HAc. On filtering,  $\text{FePO}_4$  remains upon the filter, and the filtrate contains the metal—Ba, Sr, Ca, or Mg—as chloride, and is perfectly free from phosphate.

*Method.*—Add to a portion of the cold original solution AmHO drop by drop, whilst constantly shaking the liquid, until a slight precipitate is formed which does not disappear by shaking; then add HAc and NaAc solution, and drop in  $\text{Fe}_2\text{Cl}_6$  until the liquid, after being well shaken, has a brown or red color; boil and filter immediately. The precipitate is thrown away. To the filtrate AmCl is added, then AmHO until it is just in excess, boil and filter; the liquid or filtrate, which must smell strongly of  $\text{NH}_3$ , is then tested for Ba, Sr, Ca, and Mg by (339), this liquid taking the place of the original solution.

If any precipitate is formed by  $\text{Am}_2\text{f O}_3$ , it must be well washed several times with boiling water to remove Na, since else the intense yellow coloration of Na would mask that of Ba, Sr, or Ca.

**361.** A portion of the original substance is placed in an evaporating basin, which is then nearly filled with dilute HCl, and the liquid is entirely boiled away; the dish is once more filled with acid, and again evaporated to dryness; the residue in the dish is then warmed with dilute HCl, and filtered if any residue is left:

*Solution:* the HCl solution is examined for Ba, Sr, Ca, Mg by (339), this solution being treated as is there directed for the original solution.

*Residue:* if any residue remains insoluble in HCl, it proves:

*Presence of a silicate.*

The evaporation to dryness with HCl removes  $\text{H}_3\text{BO}_3$  and HF, which volatilize, whilst  $\text{SiO}_2$  is left insoluble in HCl, and therefore remains as an insoluble powder on afterwards warming with HCl; this residue of  $\text{SiO}_2$  also remains, however, if HF was present, being caused by the corrosion of the dish; since, however, HF if present has already been found, no notice will then be taken of the residue.

## THE SUBSTANCE POSSESSES METALLIC LUSTRE.

366. This shows the probable absence of an acid-radicle. The only non-metallic elements likely to be present are free carbon as graphite, free iodine, or combined sulphur, since several sulphides are decidedly metallic in appearance.<sup>1</sup> The presence of the metals Ni, Co, Fe in the free state, and of  $\text{Fe}_3\text{O}_4$ , may be shown by the substance being attracted by a magnet. Pb, or graphite, will be recognized by marking paper when rubbed upon it, as a black-lead pencil does; the mark due to Pb disappears if wetted with dilute  $\text{HNO}_3$ .

### PRELIMINARY EXAMINATION.

Experiment.	Observation.	Inference.
I. Heat a portion of the substance in a small ignition-tube (10).	1. A black lustrous mirror forms. 2. A yellow sublimate forms, melting, when heated, to brown drops. 3. Violet vapor is given off, condensing to black scales on the sides of the tube. If the substance sublimes entirely in violet vapors.	Presence of As. Presence of S. Presence of I. Iodine alone is present.
II. Heat a portion in the inner blowpipe flame in a cavity scooped on a piece of wood-charcoal.	1. Smell of garlic. 2. If an incrustation forms, refer to par. (333,V), where in the second and third column will be found the appearance of the incrustation and the metal whose presence it indicates. 3. Smell of burning sulphur. 4. A green flame coloration,	Presence of As. Presence of S. Presence of Cu.
III. Place a portion of the substance in a piece of hard glass tube open at both ends, and heat it strongly in the Bunsen flame, and afterwards in the blowpipe flame if necessary.	1. A gas is evolved from the upper end which smells of burning sulphur and turns a piece of filter-paper moistened with $\text{K}_2\text{Cr}_2\text{O}_7$ solution green. 2. The substance burns completely but slowly away, glowing when strongly heated. This effect is best seen by heating it strongly on Pt-foil by directing the blowpipe flame on the under surface of the foil,	Presence of S. Presence of C.

<sup>1</sup> The most common sulphides which possess metallic lustre are "copper pyrites" and "iron pyrites," which resemble brass in appearance; and "galena," resembling lead.

After completing the preliminary examination proceed as directed under (332).

No acid-radicle need be tested for except S; a portion of the substance is dissolved in strong  $\text{HNO}_3$ , and after diluting with water  $\text{H}_2\text{SO}_4$  is tested for by  $\text{BaCl}_2$ ; if a white precipitate forms insoluble on boiling, it confirms the *presence of S*.

### THE SUBSTANCE IS INSOLUBLE BOTH IN WATER AND IN ACIDS.

**367.** It may consist of any one of the following substances, those included in brackets being less likely to occur than the others, since they are soluble in sufficient water or acid on heating. As will be seen below the color serves to give some notion as to what substance is present.

1. *White*:  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ , ( $\text{CaSO}_4$ ),  $\text{PbSO}_4$ , ( $\text{PbCl}_2$ ),  $\text{AgCl}$ ,<sup>1</sup>  $\text{SiO}_2$ , ( $\text{Al}_2\text{O}_3$  ignited),  $\text{SnO}_2$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_4$ ,  $\text{CaF}_2$ .
2. *Dark-colored*: ignited  $\text{Fe}_2\text{O}_3$  (dark-brown or black), ignited  $\text{Cr}_2\text{O}_3$  (dark green),  $\text{FeCr}_2\text{O}_4$ , and ignited  $\text{PbCrO}_4$  (dark brown), C (black).
3. *Yellow*: S,  $\text{AgBr}$ ,<sup>1</sup>  $\text{AgI}$ ,<sup>1</sup> ( $\text{PbI}_2$ ).

An insoluble silicate may also be present.

For a fuller description of these substances see (475).

According to the color of the substance examine it by (368 or 369).

**368.** *The substance is white.* If sufficient substance is at hand try the following preliminary tests, if not, proceed at once to (368 a). Pour upon a small portion a drop of  $\text{Am}_2\text{S}$ ; if it blackens the presence of Pb or Ag is probable, if it becomes yellow or orange-red the presence of Sn or Sb is probable; pass to Test III in the following table.

If no change of color is produced by  $\text{Am}_2\text{S}$ , try Tests I and II.

<sup>1</sup> Darkens quickly in sunlight, and slowly in ordinary daylight.

Experiment.	Observation.	Inference.
I. Moisten a clean loop of platinum wire, immerse it in the powdered substance, and heat the adhering powder for a short time strongly in the <i>inner</i> blowpipe flame; moisten the loop with a drop of strong HCl, and hold it in the Bunsen flame.	A <i>yellowish-green</i> flame.	<i>Presence of Ba.</i>
	A <i>crimson</i> flame, appearing <i>deep red</i> through the indigo-prism.	<i>Presence of Sr.</i>
	A <i>reddish</i> flame, appearing <i>dusky green</i> through the indigo-prism.	<i>Presence of Ca.</i>
		Test for $\text{SO}_4$ by Exp. 11.
II. Fuse a portion of the substance, mixed with $\text{Na}_2\text{CO}_3$ in fine powder, in a cavity scooped upon a piece of wood-charcoal, in the inner blowpipe flame, <i>produced from a spirit-lamp flame</i> .	The cooled mass, if detached from the charcoal, placed upon a bright silver coin, and moistened with water, gives, when crushed with the blade of a knife, a black stain.	<i>Presence of a sulphate.</i> <i>Note.</i> —If $\text{SO}_4$ is not found, test for F by (338 or 296), or examine the substance by (368 a).
III. Mix some of the finely powdered substance with powdered $\text{Na}_2\text{CO}_3$ and KCy, on a small cavity made in a piece of wood-charcoal, and heat the mixture in the inner blowpipe flame. If metallic globules form, detach one and strike it smartly with the pestle on the inverted mortar. Also take a globule on the point of a penknife and try if it marks paper as black lead does.	White metallic <i>malleable</i> globules, which mark paper, and if dissolved in $\text{HNO}_3$ give a white precipitate with $\text{H}_2\text{SO}_4$ ; a yellow incrustation is also formed on the charcoal.	<i>Presence of Pb</i> as chloride, sulphate, or chromate. Refer to the <i>note</i> below this table.
	White metallic <i>malleable</i> globules which do not mark paper; they dissolve in HCl, the solution giving a white precipitate with $\text{HgCl}_2$ .	<i>Presence of SnO}_2</i> .
	White metallic <i>brittle</i> globules, which if dissolved in boiling HCl, give an orange-red precipitate with $\text{H}_2\text{S}$ ; white incrustation.	
	White scales, no incrustation: the metal is insoluble in HCl, and if dissolved in $\text{HNO}_3$ gives no precipitate with $\text{H}_2\text{SO}_4$ but a white precipitate with $\text{HCl}$ ; the original substance is instantly blackened by a drop of $\text{Am}_2\text{S}$ , and is dissolved on being warmed with $\text{AmHO}$ .	<i>Presence of Sb}_2\text{O}_4 \text{ or } \text{Sb}_2\text{O}_3</i> .
		<i>Presence of AgCl.</i> [See also (368 a).]

*Note.*—Boil some of the substance with much water, add  $\text{HNO}_3$  and  $\text{AgNO}_3$ ; a white precipitate shows *presence of  $\text{PbCl}_2$* .

Test for chromate by fusing in a porcelain crucible with  $\text{Na}_2\text{CO}_3$  +  $\text{K}_2\text{CO}_3$ ; a yellow mass on cooling shows *presence of  $\text{PbCrO}_4$* .

The presence of  $\text{PbSO}_4$  may be proved by Test II, and by pouring upon the original substance  $\text{H}_2\text{A}$ , then excess of  $\text{AmHO}$ , and boiling;



the substance will dissolve; acidify a portion of the solution with  $\text{HAc}$ , and add  $\text{K}_2\text{CrO}_4$ ; a yellow precipitate: *Presence of Pb*. Acidify another portion with  $\text{HCl}$ , and add  $\text{BaCl}_2$ ; a white precipitate insoluble on boiling: *Presence of  $\text{SO}_4$* .

If none of the substances mentioned in the above table have been detected, test for  $\text{Al}_2\text{O}_3$  by heating the substance strongly on charcoal in the outer blowpipe flame after moistening it with  $\text{Co}(\text{NO}_3)_2$  solution; a blue mass shows *presence of  $\text{Al}_2\text{O}_3$* .

If  $\text{Al}_2\text{O}_3$  is not found fuse some of the substance in a clear bead of  $\text{NaAmHPO}_4$ ; it floats undissolved: *Presence of  $\text{SiO}_2$* , or a silicate. Proceed to (368 a).

**368 a.** Fuse a portion of the finely powdered substance, mixed with two or three times as much fusion mixture, for several minutes on a piece of platinum foil (or if Pb or Ag is present, in a porcelain crucible) in the blowpipe flame; boil the cool mass with water, filter and wash the residue.

*Examination of the Undissolved Residue.*—Heat the residue with dilute  $\text{HNO}_3$ ; if it is not dissolved in a short time, decant and keep the  $\text{HNO}_3$ , and heat the residue with a small quantity of dilute  $\text{HNO}_3$  and  $\text{HCl}$  mixed; if the residue is still undissolved it has been insufficiently fused.

The acid solution is then examined for the metal by (339).

*Examination of the Water Solution.*—When the metal present has been detected, it will usually be possible to limit the number of acid-radicles which need be tested for by referring to the list in (367). Tests are given below for all acid-radicles likely to occur in insoluble substances. Separate portions of the water solution are to be used.

*Sulphate:* acidify a portion with  $\text{HCl}$  and add  $\text{BaCl}_2$ ; a white precipitate.

*Chloride:* acidify a portion with  $\text{HNO}_3$  and add  $\text{AgNO}_3$ , a white precipitate easily soluble in  $\text{AmHO}$ . If the precipitate has a yellow tinge and is not easily soluble in  $\text{AmHO}$ , add to a fresh portion of the water solution dilute  $\text{Cl}$ -water drop by drop, shaking well between each

addition; a brown coloration of the  $\text{CS}_2$  shows a *bromide*, a violet coloration an *iodide*.

*Silicate*: make a portion acid with  $\text{HCl}$  and evaporate to perfect dryness; if on warming with dilute  $\text{HCl}$  an insoluble residue is left, this proves the presence of silica or a silicate.

*Fluoride*: acidify with  $\text{HAc}$  and add  $\text{CaCl}_2$ ; a gelatinous white precipitate forms. Confirm by tests (338 or 296) tried on some of the original substance.

**369.** *The substance is dark-colored.* (See 367, 2.)

Place some of the substance on a piece of platinum foil and heat the foil strongly on its under surface by the blowpipe flame:

*The substance burns away slowly but completely:*

*Presence of C.*

*The substance does not burn away; place upon it three or four times as much powdered  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$ , and fuse for some time:*

1. The substance dissolves, forming a yellow mass when cold: *Presence of  $\text{Cr}_2\text{O}_3$ .*
2. The substance remains undissolved as a dark-brown powder, and the mass on cooling is white: *Presence of  $\text{Fe}_2\text{O}_3$ .*<sup>1</sup> Confirm by boiling the mass with water, filtering and fusing the brown residue into a borax bead (100).

*The substance is yellow* (367, 3).

Heat a portion of it strongly in a small ignition-tube; one of the following results will occur:

*It fuses and sublimes, the sublimate being yellow and melting to reddish-brown drops when heated:*

*Presence of S.*

*Note.*—If the substance sublimes entirely it consists only of sulphur.

*It fuses but does not sublime*

Examine a portion of the substance for  $\text{Ag}$  and  $\text{Pb}$  and for  $\text{Br}$  and  $\text{I}$  by (368 a).

<sup>1</sup>  $\text{FeCr}_2\text{O}_4$  shows both reactions 1 and 2, since it contains both  $\text{Fe}$  and  $\text{Cr}$ .

# ANALYSES OF SIMPLE SALTS, SHOWING HOW TO ENTER RESULTS.

## A. Liquid given for analysis.

### Preliminary Examination for the Metal.

Experiment.	Observation.	Inference.
1. Noted the color of the liquid.	Blue.	Presence of Cu.
2. Dipped into it a piece of blue litmus-paper.	The paper was turned red, but on addition of $\text{Na}_2\text{CO}_3$ no effervescence occurred.	Presence of a salt with acid reaction.
3. Evaporated a few drops slowly upon a watch-glass. Ignited the residue strongly.	Pale-blue residue left. Blackened without smell of burning.	Presence of some dissolved solid. Absence of organic acid-radicles.
4. Added KHO solution and boiled.	No smell of $\text{NH}_3$ .	Absence of $\text{NH}_4$ .
5. Dipped a loop of platinum wire into the solution and held it in the flame.	<i>Bright-green</i> flame; on moistening the wire with strong HCl and again holding it in the flame it gave a blue coloration.	Presence of Cu.
6. Dipped a clear borax bead into a portion of the residue from 3. and fused in the outer and inner blowpipe flames.	In outer flame the bead was <i>green</i> whilst hot, <i>blue</i> when cold. In inner flame it became colorless.	Presence of Cu.

### Preliminary Examination for the Acid-radicle.

Experiment.	Observation.	Inference.
1. Added dilute $\text{H}_2\text{SO}_4$ and warmed.	No gas was evolved.	Absence of carbonate, sulphite, sulphide, and nitrite.
2. Added strong $\text{H}_2\text{SO}_4$ and warmed.	No gas was evolved. And no red fumes on adding Cu clippings.	Absence of chlorate. Absence of nitrate.

*Examination for the Metal.*

To a portion of the liquid added  $\text{HCl}$ :

No precipitate. Absence of Group I.	Added strong $\text{H}_2\text{S}$ -water: <i>A brownish-black precipitate. Presence of <math>\text{Sn}''</math>, <math>\text{Hg}''</math>, Bi, Pb, or Cu.</i> Allowed the precipitate to settle, poured off as much of the liquid as possible, and boiled the precipitate with excess of $\text{NaHO}$ ; it remained undissolved. Since the original solution was blue, a clean knife-blade was dipped into a portion of it acidified with $\text{H}_2\text{SO}_4$ ; red copper was deposited on the steel: <i>Presence of Cu.</i>
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*Examination for the Acid-radicle.*

- Added  $\text{HCl}$  and  $\text{BaCl}_2$ ; a white precipitate was produced which did not disappear on boiling: *Presence of Sulphate.*

*Found Cu,  $\text{SO}_4$ .*

*B. Liquid given for analysis.**Preliminary Examination for the Metal.*

Experiment.	Observation.	Inference.
1. Noted the color of the liquid.	Light yellow.	Presence of a neutral chromate.
2. Dipped red litmus-paper into the liquid.	It was turned <i>faintly</i> blue.	Probable presence of an alkali-salt.
3. Evaporated a few drops to dryness upon a watch-glass.	A yellow residue remained.	Presence of some dissolved solid.
Ignited the residue strongly.	No blackening.	Absence of organic acid-radicle.
4. Boiled a portion with excess of $\text{KHO}$ .	No smell of $\text{NH}_3$ .	Absence of $\text{NH}_4$ .
5. Dipped a loop of platinum wire into the solution, and held it in the Bunsen flame.	A pale-violet flame, appearing crimson through the indigo-prism.	Presence of K.
6. Dipped a clear borax bead into the residue from 3, and fused in the outer and inner blowpipe flames.	Outer flame: <i>brown</i> , hot; <i>green</i> , cold. Inner flame: <i>green</i> , hot and cold. <i>Brown</i> color not reappearing in the outer flame.	Presence of Cr as a chromate.

*Examination for the Metal.*

Since the liquid was alkaline in reaction, added to a small portion of it a few drops of  $\text{HNO}_3$  until it became acid; this produced no precipitate.

To another portion added  $\text{HCl}$ ; the liquid turned from yellow to orange-red, indicating presence of a neutral chromate:

No precipitate.	Then added $\text{H}_2\text{S}$ -water and warmed:		
Absence of Group I.	The liquid became green, and white S was deposited:	To another portion of the original solution added $\text{AmCl}$ , then $\text{AmHO}$ ; no precipitate formed: then added $\text{Am}_2\text{S}$ and boiled:	
	Presence of a chromate.	No precipitate in the cold, but on boiling a green flocculent precipitate gradually formed, evidently consisting of $\text{Cr}_2\text{H}_6$ reduced from the chromate.	Added to another portion of the solution $\text{AmCl}$ , $\text{AmHO}$ , and $\text{Am}_2\text{CO}_3$ :
		No precipitate. Absence of Group IV.	Added to the same portion $\text{Na}_2\text{HPO}_4$ and stirred: No precipitate. Absence of $\text{Mg}$ .

Since K was found by the flame coloration in the preliminary examination, its presence was confirmed by stirring a portion of the solution, to which a few drops of  $\text{HCl}$  had been added, with  $\text{PtCl}_4$  on a watch-glass; a yellow crystalline precipitate forming on the lines rubbed by the rod: *Presence of K.*

*Found K,  $\text{CrO}_4$ .*

*C. A white crystalline substance given for analysis.*

Boiled a small portion with water; it dissolved completely.

*Preliminary Examination for the Metal.*

Experiment.	Observation.	Inference.
1. Heated in small dry test-tube.	The substance gave off red fumes and oxygen gas, which inflamed a glowing splinter of wood. It left a yellow residue.	Presence of a nitrate of a heavy metal. Presence of Pb, Sn, or Bi.
2. Dipped a loop of moistened platinum wire into the powdered substance, moistened with strong $\text{HCl}$ and held in the Bunsen flame.	A pale-blue flame.	Presence of As, Sb, Pb.
3. Heated a small portion in a cavity on wood-charcoal in the inner blow-pipe flame.	Deflagration occurred. A white malleable globule remained which easily marked paper. A yellow incrustation.	Presence of a nitrate or chlorate.
4. Fused on charcoal in the inner blow-pipe flame with $\text{Na}_2\text{CO}_3$ and $\text{KCy}$ .	Same result as with 3.	Presence of Pb. Presence of Pb.



*Examination for the Metal in Solution.*

Boiled a portion of the powdered substance with water, cooled, added HCl to a part of the clear solution; a white precipitate was formed, which disappeared on boiling, but appeared again in the crystalline form on cooling the liquid (*probable presence of Pb*).

Confirmed the presence of Pb by decanting the liquid and boiling the precipitate with AmHO, it remained white and did not dissolve; decanted the ammoniacal liquid, dissolved the precipitate in a little  $\text{H}\bar{\text{A}}$ , and added  $\text{K}_2\text{CrO}_4$ , a yellow precipitate: *Presence of Pb*.

Since a nitrate was found in the preliminary examination, its presence was confirmed by adding strong  $\text{H}_2\text{SO}_4$  to the aqueous solution of the substance, and pouring solution of  $\text{FeSO}_4$  carefully upon the cooled liquid in a test-tube; a brown ring formed on the surface of the acid: *Presence of  $\text{NO}_3$* .

Also some of the solution when heated with Cu and strong  $\text{H}_2\text{SO}_4$ , evolved reddish-brown fumes: *Presence of  $\text{NO}_3$* .

*Found Pb,  $\text{NO}_3$ .*

*D. A white powder, emitting no smell, given for analysis.*

Boiled some of the powdered substance with water, it did not dissolve: added a few drops of strong HCl and boiled, the substance dissolved completely (absence of Group I) without effervescence.

*Preliminary Examination for the Metal.*

Experiment.	Observation.	Inference.
1. Heated in a small dry test-tube.	No change.	Absence of volatile and fusible substances and of water of crystallization, etc.
2. Dipped a moistened loop of platinum wire into the powdered substance, moistened the powder with strong HCl, and held it in the Bunsen flame.	No flame coloration.	Probable absence of K, Na, Ba, Sr, Ca, Cu, etc.
3. Heated a portion of the powder strongly on charcoal in the inner blowpipe flame.	The substance did not fuse. A white luminous residue, which when moistened on red litmus-paper showed an alkaline reaction.	Absence of alkali salt.  Presence of Ba, Sr, Ca, Mg.

*Examination of the Solution.*

To a portion of the HCl solution added  $\text{H}_2\text{S}$ -water ;  
no precipitate : *Absence of Group II.*

To another portion of the HCl solution added AmCl and AmHO in excess, a white flocculent precipitate : then added  $\text{Am}_2\text{S}$ , the color of the precipitate was unchanged.

To a few drops of the HCl solution added KHO drop by drop until a white flocculent precipitate formed, then added excess of KHO and boiled ; the precipitate did not dissolve, and it did not become discolored in the air : *Presence of Ba, Sr, Cu, Mg as phosphate, oxalate, etc.*

Added a few drops of the original HCl solution to some AmHMoO<sub>4</sub> solution in a test-tube, and warmed gently ; a yellow precipitate : *Presence of PO<sub>4</sub>.*

To another portion of the cold HCl solution added AmHO drop by drop until a precipitate formed which did not dissolve when shaken, then added HX and NaAX solution until this precipitate dissolved when the liquid was well shaken.  $\text{Fe}_2\text{Cl}_6$  was added until the liquid appeared red ; it was then boiled and immediately filtered. To the filtrate AmHO was added in excess and the precipitate filtered off, then  $\text{Am}_2\text{CO}_3$  was added ; a white precipitate formed : *Presence of Ba, Sr, or Ca.*

Filtered and dissolved the precipitate by pouring upon it a few drops of HCl ; dipped a loop of platinum wire into the solution, and held it in the Bunsen flame ; a reddish flame appearing dingy green through the indigo-prism : *Presence of Ca.*

A few drops of the solution boiled with  $\text{CaSO}_4$  gave no precipitate : absence of Ba and Sr, therefore the presence of Ca was confirmed by adding to the rest of the solution excess of AmHO, then  $\text{Am}_2\text{C}_2\text{O}_4$  ; a white precipitate : *Presence of Ca.*

*Found Ca, PO<sub>4</sub>.*

*E. A white odorless powder given for analysis.*

Boiled a portion of the substance with water, it did not dissolve : added HCl and heated again, it dissolved completely (absence of Group I) without effervescence.

*Preliminary Examination.*

Experiment.	Observation.	Inference.
1. Heated a portion in a small dry test-tube.	The substance blackened slightly; it evolved $\text{CO}_2$ , which turned a drop of lime-water milky. The residue in the test-tube effervesced with $\text{HCl}$ , whereas the original substance did not.	Presence of an organic salt of K, Na, Ba, Sr, Ca, or Mg.
2. Held a portion of the substance on a loop of platinum wire in the Bunsen flame; then moistened with $\text{HCl}$ and again held in the flame.	A red coloration, appearing <i>dusky green</i> through the indigo-prism.	Presence of Ca.
3. Heated on charcoal in inner blowpipe flame.	A white luminous mass remained, which when moistened on red litmus-paper turned it blue.	Presence of Ba, Sr, Ca, or Mg.

*Examination for the Metal.*

Added to a portion of the  $\text{HCl}$  solution strong  $\text{H}_2\text{S}$ -water.

No precipitate: Absence of Group II.	<p>To another portion of the <math>\text{HCl}</math> solution added <math>\text{AmCl}</math>, then <math>\text{AmHO}</math> in excess, a <i>white precipitate</i> formed; added <math>\text{Am}_2\text{S}</math>, the color of the precipitate remained unaltered.</p> <p>To another portion of the solution added <math>\text{KHO}</math> drop by drop until a precipitate formed, then more <math>\text{KHO}</math> and boiled; a white precipitate insoluble in <math>\text{KHO}</math>, and not darkening in the air: <i>Presence of oxalate, phosphate, etc., of alkaline earths.</i></p> <p>Since the presence of an oxalate of an alkali- or alkaline earth-metal was indicated in the preliminary examination, a portion of the original substance was heated on platinum foil, then dissolved in <math>\text{HCl}</math> (effervescence), and to the solution excess of <math>\text{AmHO}</math> and of <math>\text{Am}_2\text{CO}_3</math> was added. The liquid was warmed and put aside till the precipitate subsided, then the liquid was decanted and the precipitate dissolved in a few drops of <math>\text{HCl}</math>.</p> <p>A platinum wire dipped into this <math>\text{HCl}</math> solution gave a red flame coloration, appearing <i>dusky green</i> through the indigo-prism: <i>Presence of Ca.</i> [Confirmed by another portion of this <math>\text{HCl}</math> solution giving a white precipitate with excess of <math>\text{AmHO}</math> and <math>\text{Am}_2\text{C}_2\text{O}_4</math>.]</p>
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The presence of  $C_2O_4$  was confirmed by heating some of the original substance with strong  $H_2SO_4$ ; gases were evolved which rendered milky a drop of lime-water, and burnt with a blue flame, showing presence of  $CO_2$  and  $CO$ : *Presence of  $C_2O_4$ .*

*Found Ca,  $C_2O_4$ .*

*F. A yellow metallic-looking substance given for analysis.*

*Preliminary Examination.*

Experiment.	Observation.	Inference.
1. Heated a portion of the substance strongly in a small tube closed at one end.	A yellow sublimate formed which melted into brown drops; a smell of burning S was evolved, and a piece of paper dipped into $K_2Cr_2O_7$ solution when placed in the mouth of the tube became green. A brown residue left.	Presence of S. Probable presence of Fe.
2. Heated strongly on charcoal in the inner blowpipe flame.	Strong smell of burning S. The residue fused into a dark-colored globule, which when cold was strongly attracted by the magnet.	Presence of S.  Probable presence of Fe.
3. Heated a fragment strongly in a glass tube open at both ends, and held obliquely in the flame.	A gas was evolved with a suffocating smell, and which turned $K_2Cr_2O_7$ paper green.	$SO_2$ from combustion of S.

*Solution of Substance.*

Warmed the powdered substance with a mixture of strong  $HNO_3$  and  $HCl$ , it dissolved completely; boiled down in an evaporating-dish, adding strong  $HCl$  several times; when nearly dry, diluted with water.

*Examination of the Solution for the Metal.*

Since the substance dissolved entirely in  $HCl$ , Group I is absent; to a portion of the solution added  $H_2S$ -water:

The solution became colorless, and white S was precipitated.

*Probable presence of a ferric salt.*

To another part of the solution added  $\text{AmCl}$ , then excess of  $\text{AmHO}$ , a brown flocculent precipitate formed, *presence of  $\text{Fe}'''$* ; then added  $\text{Am}_2\text{S}$ , and heated; the precipitate became black, and on settling left a *yellow* solution: *Absence of Ni.*

Confirmed the presence of Fe by adding to a fresh part of the original solution  $\text{K}_4\text{FeCy}_6$  solution, a dark-blue precipitate: *Presence of  $\text{Fe}'''$ .*

Confirmed the presence of S by adding to a part of the original solution  $\text{BaCl}_2$ ; a white precipitate formed which did not disappear on boiling: *Presence of  $\text{SO}_4$  derived from oxidation of sulphur.*

*Found Fe, S.*

G. *A white powder given for analysis.*

Boiled a small portion with water, it did not dissolve.

Boiled another portion with  $\text{HCl}$ , it did not dissolve; added  $\text{HNO}_3$  and heated again, the substance was not dissolved. Hence the substance is insoluble in water and in acids, and, since it is white, it can only be  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ ,  $(\text{CaSO}_4)$ ,  $\text{PbSO}_4$ ,  $(\text{PbCl}_2)$ ,  $\text{AgCl}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{Sb}_2\text{O}_4$ , or  $\text{CaF}_2$ .

Poured  $\text{Am}_2\text{S}$  upon some of the substance, its color was unchanged; *probable absence of Pb, Ag, Sn, Sb.*

*Preliminary Examination.*

Experiment.	Observation.	Inference.
1. Took some of the powder up with a loop of moist platinum wire, ignited it strongly in the inner blowpipe flame, moistened it with $\text{HCl}$ , and held in the Bunsen flame.	A yellowish-green coloration.	Presence of Ba.
2. Fused a portion with $\text{Na}_2\text{CO}_3$ on charcoal in the inner blowpipe flame, placed the cooled mass on a bright shilling, and moistened it with a drop of water.	A black stain on the coin.	Presence of S.



*Examination of the Solution.*

Fused some of the powder with fusion mixture on platinum foil; boiled the cold mass with water, filtered.

*Filtrate*, made acid with HCl and added  $\text{BaCl}_2$ ; a white precipitate, which did not disappear on boiling the liquid:  
*Presence of  $\text{SO}_4$ .*

*The residue on the filter* was well washed with boiling water, and boiling dilute HCl poured upon it; it dissolved completely:

Absence of Group I.	To a portion added strong $\text{H}_2\text{S}$ -water and heated:	
No precipi- tate. Absence of Group II.	No precipi- tate.	To another portion added AmCl, then AmHO in excess, then $\text{Am}_2\text{S}$ , and boiled:
	Absence of Group III.	To another portion of the original solution added AmCl, AmHO, and $\text{Am}_2\text{CO}_3$ :
		A white precipitate: Presence of Ba, Sr, or Ca. A platinum-wire loop dipped into the original solution gave a yellowish-green tint to the Bunsen flame: <i>Presence of Ba.</i>

*Found Ba,  $\text{SO}_4$ .*

## SECTION VI.

### FULL ANALYTICAL COURSE AND TABLES.

AFTER having tried the reactions of the analytical groups and learned for each group how to detect its members occurring singly or two or more together, solutions containing a single member belonging to any of the groups, or members of two or more of these groups mixed, will readily be analyzed.

370.) *It is necessary first to separate the metals present into groups* by adding the group reagents successively in such an order that each precipitates its own group only, leaving in solution the members of all other groups which may be present. This is effected by adding the group reagents in the order directed in the general table (419); refer to this and to the group table on pp. 188, 189.

HCl, which is the first reagent added, precipitates only Group I, leaving Groups II, III, IV, and V in solution; hence if a precipitate is obtained on adding excess of HCl, after filtering it off any member or members of Group I present will be obtained upon the filter, whilst the members of all other groups remain in the filtrate. On passing  $\text{H}_2\text{S}$  into the heated filtrate,<sup>1</sup> members of Group II alone will be precipitated and may be filtered off; the filtrate,<sup>1</sup> after removal of  $\text{H}_2\text{S}$  and oxidation of any Fe present by boiling with  $\text{HNO}_3$ , may be mixed with AmCl and excess of AmHO; the AmHO will precipitate any members of Group III A, Group III B, and Mg remaining dissolved by the AmCl; the addition of  $\text{Am}_2\text{S}$  to the filtrate<sup>1</sup> will separate Group III B as sulphides. Group IV is precipitated from the filtrate<sup>1</sup> by

<sup>1</sup> Or solution, supposing no precipitate to have been obtained, and filtration therefore to have been unnecessary.

the last group reagent  $\text{Am}_2\text{CO}_3$ , and the filtrate<sup>1</sup> is examined for Group V, the members of which not being precipitated by any group reagent will now remain in solution if they were originally present.

Since each group must be *entirely* precipitated by its own group reagent it is necessary, if any precipitate is formed, to add each group reagent in "excess" before proceeding to add the next; unless the presence of the reagent in excess is ascertained before proceeding, much confusion may be caused.

**371. Addition of Reagents in Excess.**—The most general method for ascertaining the presence of a reagent in excess is to add a few drops more of the reagent to the clear liquid obtained either by letting the precipitate settle or by filtering off a small quantity of it; if any further precipitate is formed the filtered portion must be returned, more of the reagent must be added, and the clear liquid again tried with a few additional drops of the reagent, this process being repeated until no further precipitate is caused.

In certain cases this method of proceeding is rendered unnecessary, the excess of a reagent being detectable by its smell after thoroughly mixing up the solution and blowing out the air above it; this is the case for example with  $\text{H}_2\text{S}$  and  $\text{AmHO}$ . In other cases the excess is seen by the color of the filtrate, as with yellow  $\text{Am}_2\text{S}$ .

**372. Evaporation before Precipitating Group III.**—Since certain organic substances hinder or prevent the precipitation of the members of Group III A by  $\text{AmHO}$ , it is necessary, if the preliminary examination has shown the presence of organic matter, to destroy it by evaporation and ignition before proceeding to precipitate Group III; evaporation to dryness and gentle ignition are also necessary to separate  $\text{SiO}_2$ , which if remaining in solution might be mistaken for  $\text{Al}_2\text{HO}_6$ . But if it is known that neither organic substances nor  $\text{SiO}_2$  are present, a considerable saving of time may be effected by boiling the  $\text{H}_2\text{S}$  filtrate until it no longer smells of  $\text{H}_2\text{S}$ , then continuing

<sup>1</sup> Or solution, supposing no precipitate to have been obtained, and filtration therefore to have been unnecessary.

to boil for several minutes after adding a few drops of strong  $\text{HNO}_3$ ; this process may replace the evaporation to dryness and ignition.

**373. General Remarks.**—The ordinary method of analysis drawn out in the general table and in the tables for examination of the group precipitates will present little difficulty if the directions therein given are strictly complied with. Table III c will perhaps be found rather more difficult, and should not be attempted until some proficiency has been obtained by practice on the other group tables. Table III d, which must be employed under conditions fully explained in (460), should not be used until considerable proficiency has been attained.

**374.** It will be seen that the full course of analysis is arranged so as not only to prove what is present, but also that all else is absent; this, except in special cases, is the object in view.

The process of analysis is much hastened by using separate portions of the solution instead of carrying on the examination throughout with one part of the solution; the plan in the general table is however preferable, since it gives at once a notion of the relative quantities of the different substances present.

For an example of how to write out the results see pars. (488-493); it will be seen that the form adopted is that of the analytical tables.

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#### PRELIMINARY EXAMINATION OF SOLID SUBSTANCES.

**375.** Before proceeding to employ the full course of analysis for substances of complex composition, the student will do well to examine a few solid substances for metals and acid-radicles by the tables given in paragraphs (387-418).<sup>1</sup> For the full account of how to try these tests for any particular substance the student must refer back to the preceding reactions in Section IV.

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<sup>1</sup> For example of substances to be analyzed by the preliminary examinations see paragraph (538).

The results of these analyses are entered in the form of the table as shown in the examples in paragraphs (488) and (489). *The entries must be made during the progress of the analysis.*

**376. Preliminary Examination for Metals.**—A little study of this table (387 *et seq.*) will show that it contains three main tests, marked Exps. I, II, and III; these stand in the first column; in the second column are placed the results which may be noticed on trying these experiments; the student should glance through these so as to be forewarned of what he has to look for. The main classification of the results which may be observed is indicated by large-type letters, the subsidiary divisions are marked by small numbers and italics, and the individual results are simply placed in succession in a vertical column. Occasionally an observation is made which it is advisable to confirm by an additional experiment: this “confirmatory” test is then entered in the first column, just below the observation to be confirmed, and is marked “confirm” to distinguish it from the main experiment, its results are placed beside it in the second column; the student must understand that any one or more of the results noted in the second column may be looked for.

A few salts and mixtures such as those mentioned in (538) should be subjected to a careful preliminary examination by the student, and the results obtained carefully entered.

**377. Preliminary Examination for Acid-radicles.**—This table (410-418) exactly resembles in arrangement the table for metals which precedes it, and no explanation is therefore necessary. The student should examine by it some solid substances (538) for acid-radicles only.

**378.** A few solid substances may now be tested for both metals and acid-radicles by the two preliminary tables.

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DETECTION OF ACID-RADICLES AND METALS BY  
PRELIMINARY TESTS AND BY EXAMINATION OF THE  
SOLUTION.

**379.** After having become familiar with the prelimi-



nary examination of solid substances the student may analyze some easy substances containing only one or two metals and acid-radicles. The analytical course drawn out for the examination of complex substances may be at once employed for these more simple analyses, as the student is thus enabled to prove not only the presence of any particular metals or acid-radicles, but also the absence of all others.

He will by this means be gradually introduced to the analytical course, and after satisfactorily analyzing some simple substances, may proceed to mixtures of gradually increasing difficulty or complexity.

At first no mixture should be attempted which will yield a precipitate containing a phosphate in Group III, and members of Groups III A and III B should not be present together in the same solution, also substances containing organic matter and  $\text{SiO}_2$  should be avoided; the examination of the filtrate after passing  $\text{H}_2\text{S}$  is thus very much simplified.

The following is a description of the course to be pursued in making the complete analysis of a complex substance.

## GENERAL COURSE OF ANALYSIS FOR SOLID AND LIQUID SUBSTANCES.

THE substance given for analysis<sup>1</sup> will be either a liquid or a solid, since the analysis of gases forms a department which is best studied by itself.

Unless it is known that cyanogen is not present in the substance, it must be tested for in a small portion by the "Prussian blue" or AmCyS test (304 or 306; but if found, refer to (482 *et seq.*) for the preparation of the solution and the method of analysis: if cyanogen is not present the substance is examined by (380, 381) or by (382 *et seq.*), according as it is liquid or solid.

Silicates may also be tested for by fusing some of the finely powdered substance in a bead of microcosmic salt (293).

### THE SUBSTANCE IS A LIQUID.

380. Test it with both blue and red litmus-papers, one of the following results will be obtained:

<i>It is neutral</i> (not changing either paper).	<i>It is acid</i> (turning <i>blue</i> litmus <i>red</i> ).	<i>It is alkaline</i> (turning <i>red</i> litmus <i>blue</i> ).
Absence of acids and alkalies and of salts with acid or alkaline reaction. The salts of Ag and Mg and certain salts of Am, Na, K, Ba, Sr, and Ca are the only neutral soluble salts.	Presence of an acid, or salt with acid reaction.	Presence of a hydrate of Am, Na, K, Ba, Sr, or Ca, or of a salt with alkaline reaction.

381. Evaporate a few drops of the liquid upon a piece of platinum foil or a piece of thin glass or porcelain,<sup>2</sup> smelling it occasionally:

<sup>1</sup> For examples of substances to be analyzed see par. (539).

<sup>2</sup> A piece of the side of a broken flask will serve well.

*No residue is left:* The liquid must consist of some volatile substance, probably of water, either pure or containing certain gases or volatile substances dissolved in it (*e. g.*,  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{Br}$ , etc.) which are detected by their smell, by the action of the liquid on litmus-paper, or by special tests. If the liquid has no action on litmus, no smell, and leaves no residue on evaporation, and is tasteless, it is pure water.

*A residue is left:* Examine the liquid by the further preliminary tests in (334) or evaporate a portion of the solution to dryness in a porcelain dish, avoiding heating the substance after it is dry; examine the residue by the preliminary tables for metals and acid-radicles (387-418). Examine the larger part of the solution for metals by the general table (419) paying attention to (420), and the rest of the solution for acid-radicles by (440 *et seq.*).

## THE SUBSTANCE IS A SOLID.

**382.** If the substance is metallic in appearance refer to (467) for the method of analysis, or if it is non-metallic proceed as is directed below.

Finely powder some of the substance in a mortar, using an agate mortar if it is very hard. A part of this powder is first examined by the preliminary tables for metals and acid-radicles (387-418).

## PROCESS OF SOLUTION.

**383.** A large part of the remainder is boiled in a flask or boiling-tube with distilled water; if it dissolves entirely see (384); if the powder does not dissolve, allow the liquid to stand still until the undissolved portion has in great part settled, then decant through a filter: the filtrate is Solution I:

*Residue in flask:* Boil with dilute  $\text{HCl}$  (386), allow any residue to settle, decant through the filter used above (386 *a*); repeat this process and finally boil the residue with strong  $\text{HCl}$ , let settle, decant through the filter:

<i>Filtrate is</i>	<i>Residue:</i> Heat with dilute, then with strong $\text{HNO}_3$ (386 <i>b</i> ) as was directed above for $\text{HCl}$ ; decant through the filter:		
	<i>Filtrate is</i>	<i>Residue</i> may be warmed for a short time with a mixture of strong $\text{HNO}_3$ (386 <i>b</i> ) with three times as much $\text{HCl}$ ; if this does not dissolve it, dilute and decant the acid mixture through the filter:	
		<i>Filtrate is</i>	<i>Residue:</i> Wash well with water, dry, and examine as directed (475 <i>et seq.</i> ) for substances insoluble in water and acids.
Solution II.	Solution III.	Solution IV.	

384. If at any of the preceding stages the substance dissolves entirely, proceed at once to examine the solution by the general table (419), paying attention to (420) if the substance is entirely soluble in water.

385. The Solutions I, II, III, IV need rarely be examined separately; a general method is to add to I some  $\text{HNO}_3$  (see 420) and then some  $\text{HCl}$  to the clear liquid; add also to the  $\text{HNO}_3$  solution (III) some  $\text{HCl}$ . Any precipitate thus caused by  $\text{HCl}$  is examined by Table I, and any precipitate caused then on mixing the Solutions I, II, III, IV is examined by (475) as an insoluble substance. It is best to boil down the Solutions III and IV considerably before mixing them with I and II, in order to get rid of the  $\text{HNO}_3$  as much as possible; they are then mixed with dilute  $\text{HCl}$ , and any precipitate thus caused is examined by Table I.

386. Any changes which occur on adding  $\text{HCl}$  should be noted down; notice especially whether any gases are given off. Many of these gases may be detected by their smell, but a closer examination of them may be neglected, as they are obtained in the preliminary examination for acid-radicles (411). If the gases come off from the aqueous solution on adding  $\text{HCl}$ , or on mixing the  $\text{HCl}$  and aqueous solutions, they must have been present combined with metals as salts soluble in water, probably salts of alkalies; if they are evolved on treating the residue insoluble in water with  $\text{HCl}$ , they were present as salts insoluble in water.

386 a. On cooling the hot  $\text{HCl}$  solution crystals often separate; these consist probably of  $\text{PbCl}_2$ ; they may be filtered off and dissolved in a little boiling water; if on addition of  $\text{K}_2\text{CrO}_4$  to this solution a yellow precipitate forms, it shows the *presence of Pb*.

386 b.  $\text{HNO}_3$  seldom requires to be used in dissolving a substance, and when necessary should be employed only in small quantity, since it is liable to cause a precipitate of S from  $\text{H}_2\text{S}$  (423).

*Note.*—If a complex solid mixture is given for analysis, and the only object is to obtain a solution as rapidly as possible, it may be

at once boiled with aqua regia for a few minutes, then diluted and filtered: the residue is examined as a substance insoluble in water and acids (475 *et seq.*), and the filtrate is evaporated nearly to dryness: dilute HCl is added, and the solution examined by the general table (419).

## PRELIMINARY EXAMINATION FOR METALS.

**387.** The substance is required in the solid state for this examination; hence if a solution is being analyzed, some of it must be evaporated to dryness and the dry residue employed (see 381).

Carefully note down the appearance and physical properties of the original substance: whether it is crystalline or amorphous;<sup>1</sup> its hardness,<sup>2</sup> color,<sup>3</sup> smell, and anything which strikes you on a careful examination aided by a pocket lens.

The following three experiments (388, 397, 398), together with some confirmatory ones when necessary, are then to be tried on small quantities of the finely powdered substance, and the results obtained noted down.

For a fuller explanation of the form of the table, see paragraph 376.

<sup>1</sup> A body, if crystalline, consists of particles which have a definite and similar shape; the particles are amorphous if they show no similar and definite shape.

<sup>2</sup> The hardness of a substance may be roughly tested by trying to scratch it with the point of a penknife: if very easily scratched, it is soft; if the knife will not scratch it, but simply marks it as a lead-pencil would do paper, it is very hard (*e. g.*, Quartz).

<sup>3</sup> The salts of the following metals are colored: Cu, *blue*; Fe''', *brownish-yellow*; Fe'', *pale green*; Ni, Cr, CuCl<sub>2</sub>, *green*; Mn, *delicate pink*; Co, *reddish-pink*. Chromates, *light yellow*; dichromates, *orange-red*; Sb<sub>2</sub>S<sub>3</sub>, CuO, MnO<sub>2</sub>, *black*; HgO, Pb<sub>3</sub>O<sub>4</sub>, *red*; PbO<sub>2</sub>, *dark brown*; PbO, *light brown*; Cr<sub>2</sub>O<sub>3</sub>, *green*.



Experiment.	Observation.	Inference.														
388. Exp. I.—Heat a small quantity of the substance in a small test-tube or piece of hard glass tubing drawn off at one end.	A. The substance does not change.	Absence of organic substances which blacken and give off a smell of burning; of volatile substances which sublime; of substances which are altered by ignition; and of water combined with or absorbed by the substance, which would be evolved as steam and form drops on the side of the tube.														
	B. The substance changes. 1. <i>It changes color:</i> <table><tr><td>Yellow,</td><td>hot.</td><td>white, cold.</td></tr><tr><td>Yellow, brown</td><td>"</td><td>yellow,</td></tr><tr><td>Yellow-brown</td><td>"</td><td>yellow,</td></tr><tr><td>Dark red or</td><td>"</td><td>red-</td></tr><tr><td>black</td><td>"</td><td>brown</td></tr></table> The substance blackens— a. Emitting a smell of burning. The black carbon may be burnt off by strongly heating on platinum foil with the blow-pipe flame.  Smell of acetone. Smell of burning sugar. b. Emitting no smell of burning. The color is not removed by ignition as under a.  2. <i>It fuses and becomes solid again on cooling.</i>  3. <i>It sublimes.</i>	Yellow,	hot.	white, cold.	Yellow, brown	"	yellow,	Yellow-brown	"	yellow,	Dark red or	"	red-	black	"	brown
Yellow,	hot.	white, cold.														
Yellow, brown	"	yellow,														
Yellow-brown	"	yellow,														
Dark red or	"	red-														
black	"	brown														
Confirmatory.—The sublimate is carefully examined, if necessary, with the aid of a lens.	White, crystalline (sparkling) sublimate. White, non-crystalline sublimate. Black sublimate, becomes red when rubbed.  Yellow sublimate.  Sublimate of reddish drops, } which are yellow when cold. } Violet vapor, cooling to blackish crystals.															
389. Confirmatory.—Heat another portion of the substance, mixed with about three times as much Na <sub>2</sub> CO <sub>3</sub> in fine dry powder and a little KCy, in a tube closed at one end (147).	Gray mirror, which, when rubbed with a splinter of wood or a glass rod, or when examined by a lens, is seen to consist of globules of Hg. Blackish-brown shining mirror, and smell of garlic; no globules.	Presence of Hg.  Presence of As.														

Experiment.	Observation.	Inference.
390. <i>Confirmatory.</i> —Pour a little strong KHO solution upon some of the substance and heat to boiling; or mix some of the substance with soda-lime in a mortar, and moisten and heat.	$\text{NH}_3$ is given off, known by its smell and by turning moist red litmus-paper blue or turmeric-paper brown; the change in color is only a trustworthy indication, if it occurs very soon, as the $\text{NH}_3$ in laboratory air often causes it to occur after a time.	Presence of $\text{NH}_4$ .
	4. <i>The substance gives off water.</i> It fuses first, then gives off water, and again becomes solid if the heat is continued. It swells up considerably whilst giving off its water.	Presence of water, absorbed or combined. Water of crystallization.
391. <i>Confirmatory.</i> —Examine the drops of water on the sides of the tube with blue and red litmus-papers.	The water is alkaline. The water is acid.	Borax and certain borates, alums, and phosphates. Probably $\text{NH}_4$ compounds.
	5. <i>Gas or vapor is given off:</i> <i>a. It is without smell.</i>	Presence of volatile acids, <i>e. g.</i> , $\text{HNO}_3$ , $\text{HCl}$ , $\text{H}_2\text{SO}_4$ .
392. <i>Confirmatory.</i> —Introduce a burning splinter of wood into the tube.	It burns more brightly, and if introduced with a spark at the end is inflamed. The flame is extinguished.	O from chlorates, nitrates, peroxides, etc.; or possibly $\text{N}_2\text{O}$ . $\text{CO}_2$ or N.
393. <i>Confirmatory.</i> —Introduce a glass rod moistened with lime-water, into the tube.	The lime-water turns milky. The lime-water does not turn milky, but the flame was extinguished (392).	$\text{CO}_2$ from carbonates, oxalates, etc. N, from $\text{AmNO}_3$ probably.
	<i>b. The gas or vapor has a smell.</i>	
394. <i>Confirmatory.</i> —Introduce a glass rod or slip of paper moistened with $\text{K}_2\text{Cr}_2\text{O}_7$ .	Smell of burning S. The $\text{K}_2\text{Cr}_2\text{O}_7$ turns green; moist blue litmus is also reddened by the gas. Reddish-brown nitrous fumes are given off, known by their peculiar smell, and by not coloring starch paste orange-red. Smell resembling Cl:	$\text{SO}_2$ from combustion of free S, or from acid sulphites, hyposulphites, reduction of sulphates or oxidation of sulphides. Nitrates of heavy metals ( <i>e. g.</i> , of Pb, Bi, Hg, etc.).
395. <i>Confirmatory.</i> —Introduce a glass rod carrying a piece of moist litmus.	Yellowish gas, which bleaches moist litmus.	Cl from certain chlorides.
396. <i>Confirmatory.</i> —Introduce a glass rod with moist starch powder on its end.	Brown vapor, which colors the moist starch powder orange-red. Violet vapor, which colors starch solution blue.	Br from certain bromides. I, free or from certain iodides.

<sup>1</sup> This will usually be shown by effervescence of the substance; if the gas or vapor is not detected by its color or smell, it can only be found on testing for it specially by (392) and (393).

Experiment.	Observation.	Inference.
	<p><i>c. The gas can be ignited, and burns at the mouth of the tube with a: Pale yellowish-green flame, more or less explosive.</i></p> <p>Bright-white flame, producing white fumes; the unburnt gas smells of garlic.</p> <p><i>Peachblossom-colored flame.</i></p>	<p>NH<sub>3</sub> probably from strongly heated NH<sub>4</sub> NO<sub>3</sub>.</p> <p>PH<sub>3</sub> probably from a hypophosphite.</p> <p>Cy from a cyanide, probably from HgCy<sub>2</sub>.</p>
<p>397. Exp. II.—Dip a moistened loop of platinum wire, which gives no color to the Bunsen flame, into the substance, and hold the loop with the adhering powder near the top of the Bunsen flame, or in the inner blowpipe flame. Then moisten with a drop of strong HCl and heat again. Continue the heating until no further change occurs in the color of the flame.</p> <p><i>Note.</i>—If silicic acid is present, the colorations for K and Na usually show only after ignition of the powdered substance with powdered CaSO<sub>4</sub>.</p>	<p>A. The substance colors the flame:</p> <ol style="list-style-type: none"> <li>1. <i>Intense yellow.</i> Examine the flame through the indigo-prism; a crimson color is seen.</li> <li>2. <i>Pale violet, crimson through the indigo-prism.</i></li> <li>3. <i>Yellowish-green.</i></li> <li>4. <i>Crimson, same through the indigo-prism.</i></li> <li>5. <i>Orange-red, dingy-green through the indigo-prism.</i></li> <li>6. <i>Bright green.</i> A blue color is seen after moistening with strong HCl.</li> <li>7. <i>Blue.</i> { <i>Intense.</i>           <i>Livid.</i></li> </ol> <p>B. The substance does not color the flame.</p>	<p>Na.</p> <p>K or Sr, or both, are present.</p> <p>K.</p> <p>Ba probably.</p> <p>Sr.</p> <p>Ca.</p> <p>Cu or B<sub>2</sub>O<sub>3</sub>.</p> <p>Cu.</p> <p>CuCl<sub>2</sub>, CuBr<sub>2</sub>. As, Sb, Pb.</p> <p>Probable absence of the above.</p>
<p>398. Exp. III.—Heat the substance in a small cavity scooped in a piece of wood-charcoal, in the blowpipe flame.</p>	<p>A. The substance decrepitates, or crackles.</p> <p>B. The substance deflagrates, or causes charcoal to burn rapidly.</p> <p>C. The substance fuses easily, and is absorbed by the charcoal, or forms a liquid bead.</p> <p>D. An infusible residue is left on the charcoal.</p> <ol style="list-style-type: none"> <li>1. <i>The residue is white and very luminous.</i></li> </ol>	<p>NaCl and certain other crystalline salts.</p> <p>Chlorates, nitrates, etc.</p> <p>Salts of alkalies and certain salts of the alkaline earths.</p> <p>Probably BaO, SrO, CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, ZnO (or SiO<sub>2</sub>).</p> <p>BaO, SrO, CaO, and possibly MgO.</p>
<p>399. <i>Confirmatory.</i> — Detach a portion of the cool residue from the charcoal, place it upon a piece of red litmus-paper, and moisten with a drop of water.</p>	<p>The paper turns blue, showing the residue to be alkaline.</p>	

Experiment.	Observation.	Inference.
400. <i>Confirmatory.</i> —Moisten the residue on the charcoal when cool with several drops of $\text{Co}(\text{NO}_3)_2$ solution, and heat again strongly in the outer blowpipe flame.	A blue residue, the color of which does not disappear with intense heat. A pink residue. A green residue.	$\text{Al}_2\text{O}_3$ , and some phosphates, silicates, and borates. $\text{MgO}$ . $\text{ZnO}$ .
401. <i>Confirmatory.</i> —Heat a small quantity of the substance in a clear colorless borax bead, first in the outer, then in the inner blowpipe flame.	2. <i>The residue is colored.</i> Color of bead. In outer flame. In inner flame. Green, hot. } Colorless or red, } Blue, cold. } cold. } Cu. Blue, hot and cold. } Blue, hot and cold. } Co. Violet, hot. } Gray or opaque. } Ni. Yellow, cold. } Green, hot and cold. } Fe. Brown-red, hot. } Green, hot and cold. } Cr. Yellow, cold. } Green, hot and cold. } Mn. } See (402). Green, hot and cold. } (colorless, hot and cold. } Reddish-purple, hot and cold.	
402. <i>Confirmatory.</i> —The presence of Mn and Cr, may be confirmed by fusing the substance with $\text{Na}_2\text{CO}_3$ and $\text{KNO}_3$ on platinum foil.	Light-yellow mass on cooling. Blue-green mass on cooling.	Cr. Mn. (See 406.)
403. <i>Confirmatory.</i> —Heat also some of the substance, mixed or covered with powdered $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Na}_2\text{CO}_3$ or $\text{K}_2\text{C}_2\text{O}_4$ , on charcoal in the inner blowpipe flame.	3. <i>The residue is colored, or metallic scales or globules are seen.</i> The substance is reduced to the metallic state. (See 407.) a. Without incrustation. Brilliant white metal. Yellow metal. Red scales or globules. Gray powder, attracted by a magnetized knife-blade (407). b. With incrustation.	Au, Ag, Cu, Pb, Sn, Sb, Bi [Co, Ni, Fe, Mn, form gray powders]. Au, Ag, Cu, Co, Ni, Fe, Mn. Ag. Au. Cu. Fe, Co, Ni, Mn.
404. <i>Confirmatory.</i> —Detach several of the globules with the point of a knife, and strike them on the bottom of an inverted mortar with the pestle; if they flatten to a cake they are malleable, if crushed to a powder they are brittle. Try also if a globule, fixed on the point of a knife, marks paper.	Globules. Incrustation. White, malleable, not marking paper. } None or very slight. } Sn. White, brittle. } Orange, hot. } White, malleable, marking paper. } Yellow, cold. } Bi. White, brittle, giving white fumes. } Yellow, hot and cold. } Pb. White or none. } White, close to substance. } Sb. White or none. } Yellow, hot. } Zn. None. } White, cold. } Cd. None. } Red-brown, easily volatilized. } As. None. } White, and white fumes; smell of garlic.	
<i>Note.</i> —The appearance and malleability of one reduced metal is frequently much altered by the presence of another.		

Experiment.	Observation.	Inference.
405. Exp. IV. — Fuse some of the substance, mixed with $\text{Na}_2\text{CO}_3$ , on charcoal in the inner blowpipe flame <i>produced from a spirit-lamp</i> ; remove the fused mass when cold, place it on a bright-silver coin, moisten with a drop of water, and let stand for several minutes.	On rinsing off the substance, the coin is found to be stained black (408). Also, if a drop of $\text{HCl}$ be placed upon the mass, a smell of $\text{H}_2\text{S}$ is perceived, and lead-paper is blackened.	Presence of S, free or combined.  <i>Note.</i> —Since this reaction serves to detect S and sulphur acid-radicles, it more properly belongs to the preliminary examination for acid-radicles; it is, however, best tried here.

## NOTES TO THE PRECEDING PRELIMINARY TABLE.

406. The green color produced by Mn conceals the light yellow due to Cr; on boiling the residue with water it gives a pink or purple solution, the color of which is best seen on filtering; this color is due to the formation of  $\text{KMnO}_4$ , and shows Mn to be present. On acidifying this solution with  $\text{HCl}$  and boiling again for several minutes, the purple color is destroyed; and on filtering, the yellow color due to Cr is seen: the presence of Cr may be further confirmed by the formation of a yellow precipitate in the acid solution on addition of  $\text{PbA}_2$ .

407. The metal is best separated and examined by detaching the mass when cold from the charcoal, and powdering it by crushing in a mortar or on a watch-glass with a little water, letting stand for a short time, and then quickly pouring off the water down a glass rod or pestle which is wetted and pressed against its edge; by several times repeating this operation, the heavier metallic particles alone are left in the mortar or watch-glass (33 a).

408. This stain is removed by rubbing the coin with a little lime made into a paste with water.

409. *Note.*—When the substance to be examined contains several bodies, they frequently more or less mask one another's reactions: thus Co if mixed with Fe will give a bead green whilst hot and blue when cold, thus resembling Cu, but differing in remaining blue in the inner flame: hence the composition of many complex mixtures is only roughly indicated by the preliminary examination, and must be confirmed and established in the wet way. Many substances, more particularly minerals, however, can be completely analyzed by a careful preliminary examination.



## PRELIMINARY EXAMINATION FOR ACID-RADICLES.

**410.** The substance is required for this examination in the state of powder or of *strong* solution.

If the substance given for analysis is a solution, part of it may be evaporated to dryness: the dry residue is then finely powdered and subjected to the following tests. If several acid-radicles and metals are present, the reactions may be more or less perfectly concealed or altered, hence failure in obtaining a certain reaction does not in all cases necessarily prove the absence of an acid-radicle.

Experiment.	Observation.	Inference.
411. Exp. I.—Treat some of the substance with dilute HCl and note the result, then heat moderately (416).	<i>One or more of the following gases may be evolved:</i>	
	A colorless gas without smell, which turns milky a drop of lime-water on the end of a glass rod.	CO <sub>2</sub> from a carbonate.
	A gas of suffocating smell which turns a drop of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solution green. Yellow S is precipitated at the same time.	SO <sub>2</sub> from a sulphite. SO <sub>2</sub> and S from a theio-sulphate. <sup>1</sup>
	A gas with fetid odor, which blackens a drop of PbAc <sub>2</sub> solution, or a piece of lead-paper (417).	H <sub>2</sub> S from a sulphide; or possibly from a sulphite or hyposulphite, if Zn or other reducing agent be present.
	Reddish fumes.	N <sub>2</sub> O <sub>3</sub> from a nitrite.
	A yellowish-green gas, of suffocating smell, and which bleaches moist litmus-paper, is evolved:	
	a. In the cold; and also evolved on adding HAc.	Cl from hypochlorites.
	b. Only when heated.	Cl from action of HCl on oxidizing substances, e. g., MnO <sub>2</sub> , chromates, nitrates, chlorates, etc.
	A colorless gas, smelling of bitter almonds.	HCy from a cyanide.

<sup>1</sup> Formerly called a "hyposulphite."

Experiment.	Observation.	Inference.
<p>412. Exp. II. — Heat another portion gently with strong <math>\text{H}_2\text{SO}_4</math>.  <i>Note.</i>—No attention need be paid to gases evolved in Exp. I (411).</p> <p><i>Confirmatory.</i> — Mix some of the substance with <math>\text{MnO}_2</math> free from chloride, add strong <math>\text{H}_2\text{SO}_4</math> and warm.</p>	<p>1. A gas is evolved with pungent smell, which fumes in the air, and renders milky a drop of <math>\text{AgNO}_3</math> solution made acid with <math>\text{HNO}_3</math>.</p> <p>A yellow gas is given off with strong smell, and which bleaches moist litmus-paper (418). Brown vapor is given off, which colors a little moist starch powder orange-red. Violet vapor is given off, which colors a drop of starch paste blue.</p>	<p><math>\text{HCl}</math>, <math>\text{HBr}</math>, <math>\text{HI}</math>, <math>\text{HF}^1</math> from chloride, bromide, iodide, or fluoride.</p>
	<p>2. A heavy fuming suffocating gas is evolved, and the liquid behaves as if the glass were greasy; on rinsing out the tube, and drying it thoroughly, the inside is seen to be corroded and dimmed.</p>	<p>Probably <math>\text{Cl}</math> from a chloride.</p> <p><math>\text{Br}</math> from a bromide.</p> <p><math>\text{I}</math> from an iodide.</p> <p><math>\text{HF}</math> from a fluoride.  <i>Note.</i>—The <math>\text{HF}</math> acting upon the silica of the glass evolves <math>\text{SiF}_4</math>, which is detected by holding a moistened glass rod in the gas; <math>\text{SiO}_2</math> is deposited as a gelatinous film upon it.</p>
<p>413. <i>Confirmatory.</i> — Drop into the hot liquid a few small pieces of copper.</p>	<p>3. The acid fumes are reddish, usually seen only on heating after adding a few fragments of <math>\text{Cu}</math>.</p>	<p>Presence of a nitrate.  <i>Note.</i>—If iodide is present it must usually be separated by <math>\text{Cu}_2\text{SO}_4</math> (266) before a nitrate can be detected.</p>
<p>414. <i>Confirmatory.</i>—Boil some of the substance with water, or take some of the solution if a liquid; cool, add about twice as much strong <math>\text{H}_2\text{SO}_4</math>, cool, and pour cold solution of <math>\text{FeSO}_4</math> carefully in upon the top of the acid liquid.</p>	<p>A dark-brown ring or layer forms upon the surface of the acid, best obtained on cooling the liquid by immersing the test-tube in cold water.</p>	<p>Presence of a nitrate.</p>
	<p>4. Greenish-yellow gas, smelling like <math>\text{Cl}</math>, and exploding when warmed. Confirm by adding indigo solution and <math>\text{H}_2\text{SO}_4</math> to the colorless aqueous solution of the substance (252). For detection of a nitrate and chlorate when mixed, see (256).</p>	<p>Presence of a chlorate.</p>
	<p>5. The substance changes from yellow to green, <math>\text{O}</math> being evolved as is shown by a glowing taper.</p>	<p>Presence of a chromate.</p>

<sup>1</sup>  $\text{HF}$  would also render the drop milky by depositing  $\text{SiO}_2$  from  $\text{SiF}_4$ , formed by its action on the glass, but it is distinguished by corroding the glass. (See 412, 2, note.)

Experiment.	Observation.	Inference.
	6. Yellowish-green gas, with suffocating smell, which bleaches moist litmus.	Cl from a hypochlorite (detected already in 411), or from a chloride in presence of $\text{MnO}_2$ , etc.
	7. The same gas as in 6, but colored reddish-brown by nitrous fumes:	A chloride in presence of a nitrate or nitrite.
	8. Or colored reddish-brown by $\text{CrOCl}_2$ .	A chloride in presence of a chromate.
	9. Substance does not blacken, but evolves $\text{CO}$ , which burns with a blue flame, and $\text{CO}_2$ , which turns a drop of lime-water milky.	Presence of an oxalate.
	10. Substance blackens, and $\text{SO}_3$ is smelt.	Presence of a tartrate.
	11. A smell of acetic acid or vinegar is noticed.	$\text{H}\bar{\text{A}}$ from an acetate.
415. <i>Confirmatory</i> .—Add a little alcohol to the substance and heat with $\text{H}_2\text{SO}_4$ .	Strong fragrant odor.	Ethyl-acetate from an acetate.

## NOTES ON THE PRECEDING TABLE.

**416.** If  $\text{HCl}$  has been employed in dissolving the substance, the acid-radicles detected by the action of  $\text{HCl}$  will have been already noticed in preparing the solution for metals (383).

**417.** The S present in sulphides which are not decomposed by dilute  $\text{HCl}$ , is detected by fusing the powdered substance with two or three times as much fusion mixture ( $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ ) in a covered crucible, boiling with a little water, and placing a drop upon a bright silver coin, when a dark stain will be produced; or by adding excess of an acid to the solution, when  $\text{H}_2\text{S}$  will be evolved. Smaller quantities of S may be detected by the formation of a black color or precipitate on adding  $\text{PbA}_2$  to the solution.

**418.** Chlorides treated in this manner evolve Cl, recognized by its color, smell, and bleaching action on litmus-paper; but this test for chlorides is reliable only if the precautions stated in (259) are attended to, since many samples of  $\text{MnO}_2$  evolve Cl when warmed alone with  $\text{H}_2\text{SO}_4$ .

## EXAMINATION FOR METALS.

After the preceding preliminary examinations have been made, a solution of the substance is made as directed in (383 *et seq.*), and this solution is further examined in a more systematic manner. This is often called "The Examination in the Wet Way." See next page.

## 419. GENERAL TABLE FOR SEPARATION OF

If the substance for analysis is a liquid with neutral or *alkaline* reaction, examined as directed below.

In this table, and also in the group tables which follow, it has been supposed that a precipitate will be produced when the reagent is added for its detection; and

Add to the greater part of the "original solution" <sup>1</sup> HCl; if any precipitate is produced						
<p>The precipitate may contain—</p> <p>PbCl<sub>2</sub>—<i>white</i>.  AgCl—<i>white</i>.  Hg<sub>2</sub>Cl<sub>2</sub>—<i>white</i>.  (See 422.)</p>	<p>The filtrate or solution, which must give no further precipitate when diluted with water (425), unless it is already diluted, warmed gently (426, 426 a) and filtered:</p>					
<p>Examine the precipitate by Table I (433).</p>	<p>The precipitate may contain—</p> <table border="0"> <tr> <td> <p>HgS—<i>black</i>  PbS—<i>black</i>  Bi<sub>2</sub>S<sub>3</sub>—<i>black</i>  CuS—<i>black</i>  CdS—<i>yellow</i></p> </td> <td> <p>} Insoluble in KHO and in Am<sub>2</sub>S.</p> </td> </tr> <tr> <td> <p>SnS—<i>brown</i>  SnS<sub>2</sub>—<i>yellow</i>  Sb<sub>2</sub>S<sub>3</sub>—<i>orange</i>  As<sub>2</sub>S<sub>3</sub>—<i>yellow</i>  [Au<sub>2</sub>S<sub>3</sub>—<i>black</i>]  [PtS<sub>2</sub>—<i>black</i>]</p> </td> <td> <p>} Soluble in KHO and in Am<sub>2</sub>S.</p> </td> </tr> </table>	<p>HgS—<i>black</i>  PbS—<i>black</i>  Bi<sub>2</sub>S<sub>3</sub>—<i>black</i>  CuS—<i>black</i>  CdS—<i>yellow</i></p>	<p>} Insoluble in KHO and in Am<sub>2</sub>S.</p>	<p>SnS—<i>brown</i>  SnS<sub>2</sub>—<i>yellow</i>  Sb<sub>2</sub>S<sub>3</sub>—<i>orange</i>  As<sub>2</sub>S<sub>3</sub>—<i>yellow</i>  [Au<sub>2</sub>S<sub>3</sub>—<i>black</i>]  [PtS<sub>2</sub>—<i>black</i>]</p>	<p>} Soluble in KHO and in Am<sub>2</sub>S.</p>	<p>The solution or filtrate is precipitated: as soon as the dish until it ceases to smoke, and the residue gently heated, then water is added.</p> <p>Add a few drops of the acid; the precipitate shows the presence of the acid.</p> <p>Add to the rest of the HCl solution once any precipitate which (429): if a phosphate is present, phosphates are absent proceed as follows.</p> <p>[Note.—Refer to Table I (433).]</p>
<p>HgS—<i>black</i>  PbS—<i>black</i>  Bi<sub>2</sub>S<sub>3</sub>—<i>black</i>  CuS—<i>black</i>  CdS—<i>yellow</i></p>	<p>} Insoluble in KHO and in Am<sub>2</sub>S.</p>					
<p>SnS—<i>brown</i>  SnS<sub>2</sub>—<i>yellow</i>  Sb<sub>2</sub>S<sub>3</sub>—<i>orange</i>  As<sub>2</sub>S<sub>3</sub>—<i>yellow</i>  [Au<sub>2</sub>S<sub>3</sub>—<i>black</i>]  [PtS<sub>2</sub>—<i>black</i>]</p>	<p>} Soluble in KHO and in Am<sub>2</sub>S.</p>					
<p>Note.—The absence of Pb is not proved if it is not precipitated in this group, as PbCl<sub>2</sub> is somewhat soluble, and Pb may therefore be found only in Group II.</p>	<p>Examine the precipitate by Table II (435).</p> <p>Note 1.—This precipitate should not be examined at once, as possibly a precipitate may be formed on boiling the filtrate, and this would have to be added to the above.</p> <p>Note 2.—Unless the liquid has been sufficiently diluted some of the above metals may be afterwards precipitated by Am<sub>2</sub>S in Group III, and cause much confusion.</p>	<p>The precipitate may contain—</p> <p>Al<sub>2</sub>HO<sub>3</sub>—<i>almost colorless</i>.  Cr<sub>2</sub>HO<sub>3</sub>—<i>light green</i>.  Fe<sub>2</sub>HO<sub>3</sub>—<i>reddish-brown</i>.</p> <p>Examine the precipitate by Table III A (436).</p>				

## NOTES TO THE GENERAL TABLE.

420. If the liquid under examination is alkaline or neutral in reaction, before commencing the examination by the general table,  $\text{HNO}_3$  must be added in slight excess; if no precipitate forms, proceed at once to examine the liquid by the general table; if a precipitate is produced, more  $\text{HNO}_3$  is to be added, and the liquid heated;

<sup>1</sup> By the "original solution" is meant the solution of the substance if a solid, or the substance itself if a liquid, to which no reagent has been added.



## METALS INTO GROUPS BY GROUP REAGENTS.

requires special treatment (420); if its reaction is *acid*, it may be at once posed that all metals are present; if a metal or group of metals is absent, no hence no filtration is necessary, the solution being then treated as a filtrate.

continue to add HCl as long as it causes any further precipitate (421), warm and filter:

tate on addition of several drops of HCl, is boiled down if necessary (423), and is it is then saturated with  $H_2S$  by passing the gas through the solution<sup>1</sup> (500 a), and

luted and  $H_2S$  is passed again into it, to make sure that Group II is completely pre- produces no further precipitate the clear solution or filtrate is boiled in a porcelain of  $H_2S$  (427), a little strong  $HNO_3$  is then added, and the liquid is evaporated to dryness nited in the dish. When the dish is cool, a little strong HCl is poured upon the residue added; any undissolved residue is filtered off (428).

solution to some  $AmHMoO_4$  solution in a test-tube, and warm gently; a yellow precipi- phosphate; if no precipitate is formed with  $AmHMoO_4$ , phosphates are absent.

tion  $AmCl$ , heat it to boiling, then add  $AmHO$  in excess, boil again and filter off at may form as quickly as possible, keeping the funnel closely covered with a glass plate present and a precipitate is produced by  $AmHO$  refer to Table III b (466), if phos- is directed below:

(463 *et seq.*), for full directions for precipitating Groups III A and III B.]

Add to the filtrate or solution, which may be colored (430),  $Am_2S$  in excess, boil and filter:

The precipitate may contain—

$ZnS$ —white.  
 $MnS$ —light pink.  
 $CoS$ —black.  
 $NiS$ —black.

Examine this precipitate at  
*once* by Table III b (437).

Add to the filtrate or solution, which must be distinctly yellow or brown (431),  $Am_2CO_3$ , warm gently and filter:

The precipitate (432) may  
 contain—

$BaCO_3$ —white.  
 $SrCO_3$ —white.  
 $CaCO_3$ —white.

Examine the precipitate  
 by Table IV (438).

The filtrate may contain  
 $Mg$ ,  $K$ ,  $Na$ .

Examine by Table V  
 (439).

should a precipitate still remain, it is filtered off and the filtrate ex- amined by the general table, commencing with the addition of HCl.

The precipitate caused and not dissolved by  $HNO_3$  may be finely divided sulphur, separated as a *white* powder from a sulphide, or *yellow* from a thiosulphate;<sup>2</sup> this precipitate is recognized by its color, and by not being separable by standing or filtration, it may be disregarded; there may also be precipitated  $H_2SiO_3$  (gelatinous,

<sup>1</sup> Instead of diluting and passing the gas,  $H_2S$  solution may be added

<sup>2</sup> Often called a "hyposulphite."

almost colorless),  $\text{SnO}_2$  or metastannic acid (see 420 a),  $\text{Sb}_2\text{O}_5$ ,  $\text{AgCl}$  (all three white),  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_3$  (both yellow),  $\text{Sb}_2\text{S}_3$  (orange). Hence a full examination of this precipitate for all that it may contain will involve boiling the precipitate with aqua regia, diluting and filtering; the insoluble residue is examined as a substance insoluble in water and acids (475), and the aqua regia solution is added to the filtrate from the precipitate caused by  $\text{HNO}_3$ , any precipitate caused on thus mixing the solutions being examined by Table I (433).

**420 a.** Metastannic acid is precipitated from a solution of an alkaline metastannate by addition of an acid; it forms a white precipitate which becomes *golden-yellow* when moistened with  $\text{SnCl}_2$  solution; it is further recognized by its dissolving in the washing-water whilst being washed, but being reprecipitated when the washings run into the acid filtrate.

**421.** Even if  $\text{HCl}$  has been used in dissolving the substance, it is advisable to add a few drops of the acid to make sure that no member of Group I remains.

**422.** It must be remembered that  $\text{HCl}$  also precipitates strong Ba solutions; this precipitate, however, disappears as  $\text{PbCl}_2$  does on diluting with water and heating, thus differing from  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$ .

**423.** If  $\text{HNO}_3$  or aqua regia has been used in dissolving the substance, or if the solution smells of  $\text{Cl}$  or  $\text{SO}_2$ , it should be boiled down considerably until after adding  $\text{HCl}$  and boiling, neither of the above gases is smelt; it is then diluted, and  $\text{H}_2\text{S}$  passed at once whether the dilution has caused any precipitate or not.

If As has been detected in the preliminary examination,  $\text{H}_2\text{SO}_3$  should be added until the liquid smells of  $\text{SO}_2$  after having been boiled for a short time, and the liquid is then heated for some time short of boiling, until it no longer smells of  $\text{SO}_2$ . This treatment reduces arsenic and stannic compounds to the arsenious and stannous condition. In the case of As this reduction is to be recommended, since arsenic compounds are not easily precipitated by  $\text{H}_2\text{S}$ ; it is also very desirable to reduce stannic compounds, since  $\text{SnS}_2$  unlike  $\text{SnS}$  readily runs through the filter, and being yellow in color may be mistaken for S. It will of course be necessary to ascertain by special tests (187-190, and 201-203), made on the *original solution*, in which state As and Sn were originally present. If any precipitate is produced by boiling with  $\text{H}_2\text{SO}_3$  other than white sulphur, refer to 424.

**424.** Whilst boiling with  $\text{H}_2\text{SO}_3$  some  $\text{H}_2\text{SO}_4$  is usually formed, which may partially or completely precipitate Pb, Ba, Sr as white sulphates;  $\text{H}_2\text{SO}_3$  will also possibly precipitate Au, which causes the cool liquid to appear blue by transmitted and red by reflected light, and on boiling separates as a black powder. Examine any precipitate formed by  $\text{H}_2\text{SO}_3$  by Table G (434).

**425.** On addition of water, Bi, Sb, Sn may give white precipitates of their oxychlorides; these precipitates may be disregarded, since  $\text{H}_2\text{S}$  readily converts them into sulphides.

**426.**  $\text{H}_2\text{S}$  often causes a fine *white* precipitate of S, owing to the presence of certain oxidizing substances, such as  $\text{Cl}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_3$ ,  $\text{H}_2\text{CrO}_4$ ,  $\text{H}_2\text{MnO}_4$ ,  $\text{HMnO}_4$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{Fe}_2\text{Cl}_6$ , etc.; this precipitate is known by its perfect whiteness, and by not being separable by standing or filtration, it may be neglected; great care must however be

taken not to mistake  $\text{SnS}_2$  for S; it resembles S in running through filter-paper, but is distinctly *yellow* in color; it may often be coagulated by being shaken or heated.

**426 a.** Certain changes may be observed whilst  $\text{H}_2\text{S}$  is being passed; they should be carefully noted. Thus Pb and Hg during precipitation by  $\text{H}_2\text{S}$  show characteristic colors (149, 144); a solution colored reddish-yellow by  $\text{H}_2\text{CrO}_4$  becomes green; and a solution colored green by  $\text{H}_2\text{MnO}_4$  or purple by  $\text{HMnO}_4$  becomes colorless.

**427.** If on boiling the filtrate or solution after passing  $\text{H}_2\text{S}$  a yellow precipitate forms, this shows the presence of an arsenic or a stannic compound; in this case pass  $\text{H}_2\text{S}$  into the boiling liquid as long as it causes any further precipitate, filter off and add this precipitate to any precipitate already obtained by  $\text{H}_2\text{S}$  to be examined by Table II.

**428.**  $\text{SiO}_2$  and other substances may be present in this residue, but  $\text{SiO}_2$  is distinguished from them all by readily dissolving in hot  $\text{KHO}$  solution.

The other substances which may remain undissolved by  $\text{HCl}$  are  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , rendered difficultly soluble by the ignition to which the residue has been subjected; they are dissolved by long-continued heating with strong  $\text{HCl}$ , and the solution is added to the other solution which is to be examined for Group III A.

$\text{BaSO}_4$  and  $\text{SrSO}_4$  may also remain undissolved; they are detected by heating some of the residue strongly for a short time in the inner blowpipe flame upon a loop of platinum wire, then moistening the loop with a drop of strong  $\text{HCl}$  and holding it in the outer part of the Bunsen flame; crimson-red flashes appearing red through the indigo-prism prove the presence of Sr; a yellowish-green flame coloration shows Ba.

A less ready method of detecting Ba and Sr is to dry the insoluble residue, fuse it on platinum foil with three or four times as much fusion mixture; allow it to cool, then boil with water until the mass is disintegrated, filter, wash the residue well upon the filter, and examine it by Table IV (438) for Ba and Sr only.

**429.** Mn and Zn are very liable to be precipitated with  $\text{Fe}_2\text{HIO}_6$ ,  $\text{Al}_2\text{HIO}_6$ ,  $\text{Cr}_2\text{HIO}_6$ . The precipitation of Mn is partly prevented by keeping the liquid from exposure to the air after adding  $\text{AmHIO}$ ; but the further precaution should be taken of dissolving the precipitate produced by  $\text{AmHIO}$  in  $\text{HCl}$  and reprecipitating it by  $\text{AmHIO}$ , then filtering and adding the filtrate to the original filtrate from the Group III A precipitate; this treatment of the precipitate should be repeated several times, if small quantities of Zn or Mn have to be looked for in presence of Al or Fe; or better still Groups III A and III B may be precipitated together (459) and the precipitate examined by Tables III c (464, 465). See rules (463).

**430.** The filtrate or solution, after adding  $\text{AmCl}$  and  $\text{AmHIO}$ , may be colored *blue* by Ni, or *reddish-violet* by  $\text{Cr}_2\text{HIO}_6$  which is dissolved in the excess of  $\text{AmHIO}$ .

The  $\text{Cr}_2\text{HIO}_6$  must be removed before proceeding to examine for the three remaining groups; it is readily separated as a pale-green flocculent precipitate by boiling the liquid for a short time in a porcelain

dish, adding a little more  $\text{AmHIO}$  if the liquid does not smell of  $\text{NH}_3$  after being boiled for a short time; this precipitate is filtered off, and the filtrate, which is colorless if the Cr has been entirely removed by boiling the liquid sufficiently long, is further examined for Groups III B, IV, and V by the general table.

The coloration due to Ni differs from that caused by  $\text{Cr}_2\text{HO}_6$  in not being thus removed by boiling the liquid.

**431.** A *brown or dark-colored* filtrate shows that Ni is present,<sup>1</sup> some of the NiS precipitated by  $\text{Am}_2\text{S}$  having been dissolved in the excess of  $\text{Am}_2\text{S}$  and giving the filtrate its dark color. If this coloration is noticed the filtrate should be poured into a porcelain dish and boiled, occasionally adding water if necessary, until on removing the lamp for a short time the black NiS settles, leaving a colorless liquid. The liquid is then run through a small filter, and the black precipitate tested for Ni by fusing a portion of the filter-paper stained by the NiS in a colorless borax bead; if a bead is obtained, which when heated in the outer flame is *violet or brown* whilst hot, and *yellow* when cold, and *which becomes gray or opaque in the inner flame*, Ni is certainly present and need not be further tested for in Table III B.

The colorless filtrate is examined by the general table for Groups IV and V.

**432.** Part of the precipitate produced by  $\text{Am}_2\text{CO}_3$  often adheres firmly to the inside of the vessel in which it has been produced; in this case rinse the tube out several times with distilled water and then dissolve the precipitate by pouring in some hot HCl, causing it to run over the inside of the tube, and add this solution to the HCl solution of the  $\text{Am}_2\text{CO}_3$  precipitate made in Table IV.

<sup>1</sup> If Groups III A and III B have been precipitated together by  $\text{AmCl}$ ,  $\text{AmHIO}$ , and  $\text{Am}_2\text{S}$  added in succession (459) the brown coloration of the filtrate may also be due to  $\text{Cr}_2\text{HO}_6$ : on boiling the filtrate colored by  $\text{Cr}_2\text{HO}_6$  in a porcelain dish for several minutes, *pale-green*  $\text{Cr}_2\text{HO}_6$  is precipitated, which cannot be mistaken for *black* NiS.

## 433. TABLE I.—SILVER GROUP.

The precipitate produced by  $\text{HCl}$  may consist of  $\text{PbCl}_2$ ,  $\text{AgCl}$ , and  $\text{Hg}_2\text{Cl}_2$ : the precipitate on the filter is washed five or six times with boiling water, the first portions of the washings being kept apart:

<p>The first portions of the washings may contain <math>\text{PbCl}_2</math> in solution, which if present in any quantity will be deposited in brilliant crystals on cooling.</p> <p>Test for, or confirm the presence of, <math>\text{Pb}</math>, by adding to the washings <math>\text{K}_2\text{CrO}_4</math>: a yellow precipitate readily soluble in <math>\text{KHO}</math> shows:</p> <p><i>Presence of Pb.</i></p>	<p><i>Residue:</i> pour upon the precipitate on the filter some hot <math>\text{AmHO}</math>; when this has run through, heat it again, and pour it once more upon the filter.</p> <p><i>Filtrate:</i> add <math>\text{HNO}_3</math> until the liquid is acid; a white precipitate uniting into curdy particles when shaken or boiled shows:</p> <p><i>Presence of Ag.</i></p>	<p><i>Residue</i> on the filter is black; dry at a gentle heat, best in a steam-bath; scrape the precipitate off the filter, mix with some dry <math>\text{Na}_2\text{CO}_3</math>, and heat in a small ignition-tube (147). Globules of <math>\text{Hg}</math> form on the sides of the tube, often appearing only when the inside of the tube is rubbed or examined with a lens:</p> <p><i>Presence of Hg' (Mercurousum).</i></p>
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434. TABLE G.—EXAMINATION OF THE PRECIPITATE FORMED ON BOILING THE  $\text{HCl}$  SOLUTION WITH  $\text{H}_2\text{SO}_3$ . (See par. 424.)

The precipitate produced by  $\text{H}_2\text{SO}_3$  may contain  $\text{Au}$ ,  $\text{PbSO}_4$ ,  $\text{BaSO}_4$ , and  $\text{SrSO}_4$ ; the last three substances are perfectly white, and  $\text{Au}$ , if present, is therefore usually seen by coloring the precipitate brown or black: the  $\text{Au}$  is also usually visible during precipitation by  $\text{H}_2\text{SO}_3$ , or after the white sulphates have subsided, since it colors the liquid blue by transmitted and reddish by reflected light.

$\text{Ba}$  and  $\text{Sr}$  can often be at once detected, if present, by taking a little of the moist precipitate on a loop of platinum wire, heating in the inner blowpipe flame for some time, moistening with  $\text{HCl}$ , and examining the flame coloration; but a more trustworthy method of proceeding is the following:

Rinse the precipitate into a small porcelain dish, using as little water as possible; dissolve in the liquid a small crystal of  $\text{H}_2\text{T}$  or add a few drops of strong  $\text{HA}$ ; then add  $\text{AmHO}$  until it is just in excess, and boil for a short time; let stand and decant through a filter:

<p><i>Solution</i> may contain <math>\text{PbSO}_4</math>; add <math>\text{HA}</math> in excess, then <math>\text{K}_2\text{CrO}_4</math>; a yellow precipitate soluble in <math>\text{KHO}</math> shows:</p> <p><i>Presence of Pb.</i></p>	<p><i>Residue:</i> pour upon the residue in the dish a little <math>\text{HCl}</math> and a few drops of <math>\text{HNO}_3</math>, heat to boiling, let stand, decant into a porcelain dish:</p> <p><i>Solution:</i> boil until the smell of <math>\text{Cl}</math> is removed; add several drops of fresh <math>\text{FeSO}_4</math> solution; a blue coloration and reddish precipitate show:</p> <p><i>Presence of Au.</i></p>	<p><i>Residue:</i> dry by gently heating the dish, fuse with fusion mixture on platinum foil, and examine the mass for <math>\text{Ba}</math> and <math>\text{Sr}</math> as directed in the last part of (428).</p>
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## 435. TABLE II.—COPPER AND

The precipitate produced by  $H_2S$  in the  $HCl$  solution, after of the washing-water, collected in a test-tube, give no precipitate from the filter and boiled with  $KHO$  or a small quantity of  $Am_2S$ .

## GROUP II A.—COPPER GROUP.

435 a. The residue may contain  $H_2S$ ,  $PbS$ ,  $Bi_2S_3$ ,  $CuS$ ,  $CdS$ . After having washed the precipitate and allowed it to drain, remove it from the filter into a porcelain dish 26 d. pour upon it strong  $HNO_3$  sufficient to cover it completely, and heat gently as long as any effumes come off, adding more strong  $HNO_3$  if necessary to prevent evaporation to dryness. Boil off nearly all the acid, add a little water and dilute  $H_2SO_4$ , let stand for some time stirring occasionally, and filter;

Residue may contain  $HgS$  (black),  $PbSO_4$  (white), see Note 1.

Remove the precipitate into a porcelain dish, using as little water as possible; add a little  $HA$ , then  $AmHO$  in excess, boil and filter;

Residue: dry on the filter at a gentle heat, best in the steam oven. Scrape the dried residue off the filter (Note 2), and heat it, mixed with dry  $Na_2CO_3$ , in a small ignition-tube; globules of  $Hg$  form on the sides of the tube, which become visible when rubbed or when looked for by a lens:  
Presence of  $Hg''$  (Mercuricum).

Filtrate: Add  $HA$  in excess, then  $K_2CrO_4$ , a yellow precipitate:

Presence of  $Pb$ .

Filtrate may contain  $Bi$ ,  $Cu$ ,  $Cd$ .

Add  $AmHO$  in excess, boil and filter:

[Note.—A blue coloration shows presence of  $Cu$ .]

Precipitate (not easily seen in dark-blue solutions); wash with hot water, dissolve off the filter by pouring upon it a few drops of boiling dilute  $HCl$ , pour this solution into a large quantity of cold distilled water, a milkiness appearing at once or after stirring and letting stand for some time, shows:

Presence of  $Bi$ .

Note.—A precipitate produced by  $AmHO$  must always be tested as above for  $Bi$ , since  $Pb$  and  $Hg$  might possibly appear here as white precipitates and be mistaken for  $Bi$ .

Filtrate: add  $HCl$  until the liquid is acid, then pass  $H_2S$  to saturation, filter and wash quickly, keeping the filter covered with a glass plate; rinse the precipitate into a test-tube, pour upon it some dilute  $H_2SO_4$ , boil and filter through a covered filter (Note 3):

Residue: dissolve by pouring a little boiling  $HNO_3$  upon the filter, add to the solution  $AmHO$  in excess, then  $HA$  in excess, and a few drops of  $K_4FeCy_6$ : a chocolate-red precipitate shows:

Presence of  $Cu$ .

Filtrate: add much water and pass  $H_2S$  for some time (or add neutral  $H_2S$ -water), a yellow precipitate shows:

Presence of  $Cd$ .  
Note.—If this precipitate is dark-colored,  $CuS$  is present (see Note 3), filter it off, boil it once more with  $H_2SO_4$ , filter and test the filtrate by  $H_2S$  as above, for  $Cd$ .

Note 1.—A white residue does not necessarily show the absence of  $Hg$ .

Note 2.—If the amount of the residue is too small to be removed the portion of the paper containing it may be cut up and mixed with  $Na_2CO_3$ . For the precautions requisite in performing this test see (147).

Note 3.—Unless this precipitate is filtered in a covered funnel, washed quickly, and examined at once,  $CuS$  is liable to be oxidized and to pass into the filtrate as  $CuSO_4$ ; it then discolors the  $CdS$  precipitate, or may be entirely overlooked if present in small quantity.

If traces of  $Cu$  have to be tested for,  $Na_2S$  should be substituted for  $Am_2S$ , since  $CuS$  is somewhat soluble in  $Am_2S$ ; but  $Sn''S$  and  $Au_2S_3$  are much more readily soluble in  $Am_2S$ .

## ARSENIC GROUPS.

having been well washed with hot water until the last few drops leave only a very slight milkiness on addition of  $\text{AgNO}_3$ , is removed and filtered:

## GROUP II B.—ARSENIC GROUP.

*The filtrate may contain  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}_2$ ,  $\text{SnS}$ ,  $[\text{Au}_2\text{S}_3$ ,  $\text{PtS}_2]$ . Add to it  $\text{HCl}$  until it is acid, and pass  $\text{H}_2\text{S}$  unless the liquid smells strongly; the above sulphides if present will be reprecipitated; a mere milkiness due to precipitation of S may be disregarded.*

*The precipitate is filtered off and examined as directed in 435 b (see Note 4, below):*

**35 b.** Remove the precipitate from the filter into a porcelain dish, using as little water as possible; add a little strong  $\text{HCl}$  and heat, occasionally dropping in a crystal of  $\text{KClO}_3$ , until the precipitate dissolves entirely, or leaves only a slight residue of sulphur. Heat this solution just short of boiling (Note 5) until it ceases to smell of  $\text{Cl}$  (Note 6), then cool it and pour it, through a filter if necessary, into a small flask (181) containing pieces of pure  $\text{Zn}$ : if the gas does not come off readily, add a little strong  $\text{HCl}$ , and cause the gas after passing through some  $\text{PbAc}_2$  solution (see caution 181) to bubble through some  $\text{AgNO}_3$  solution contained in a broad test-tube. As soon as the evolution of gas slackens, drop in more  $\text{Zn}$ , unless some remains undissolved in the flask, and as soon as the gas ceases to come off, some  $\text{Zn}$  still remaining undissolved, remove the test-tube containing the  $\text{AgNO}_3$  solution; if any black precipitate has formed in this solution it must be examined as below; if the liquid has remained clear and colorless it may be rejected, since  $\text{As}$  and  $\text{Sb}$  are absent.

*Residue in the flask may consist of  $\text{Sn}$  ( $\text{Pt}$ ,  $\text{Au}$ ), and excess of  $\text{Zn}$ ; remove any deposit of  $\text{Sn}$  by shaking the pieces of  $\text{Zn}$  well with the liquid and quickly pouring off into a dish, decant the liquid and wash the  $\text{Sn}$  by decantation in the dish; boil the residue with a little strong  $\text{HCl}$  in a test-tube, then quickly dilute, decant (Note 7), and add  $\text{HgCl}_2$  to the solution; a white precipitate, becoming black with  $\text{AmHO}$ , shows:*

*Presence of  $\text{Sn}$  (Note 8).*

*To the liquid in the test-tube add several drops of  $\text{AgNO}_3$  solution, filter:*

*Precipitate:* wash well with boiling water until  $\text{HCl}$  gives no milkiness with the last few drops of the washing-water, then pour upon the filter a little boiling dilute  $\text{H}_2\text{T}$  solution, boil it and pour it again through the filter; repeat this several times, then add to the solution  $\text{HCl}$  and pass  $\text{H}_2\text{S}$ ; an orange-red precipitate shows:

*Presence of  $\text{Sb}$ .*

*Note.*—This precipitate is often only seen on settling from the yellow liquid.

*Filtrate:* dilute several drops of  $\text{AmHO}$  largely in a test-tube and add this liquid drop by drop to the filtrate: a light-yellow precipitate which settles in flocks on shaking the liquid shows:

*Presence of  $\text{As}$  (Note 8).*

It is well to pour a few drops of  $\text{H}_2\text{S}$ -water into the funnel with each fresh addition of washing-water.

*Note 4.*—The detection of  $\text{As}$ ,  $\text{Sb}$ ,  $\text{Sn}$  by the method given in (435 b) is very trustworthy and delicate (208); it is excelled in these respects by the method in (210). For beginners, however, the process (209) is recommended by its greater simplicity.

*Note 5.*—The solution must not be heated to boiling, else  $\text{SbCl}_3$  or  $\text{SnCl}_4$  might be volatilized if present.

*Note 6.*—In this solution  $\text{As}$  and  $\text{Sn}$  will be present as stannicium, and arsenicium, and in this state are not well suited for detection: the following modification makes their detection much more rapid and certain, especially when they are present only in small quantity. After

warming until the liquid ceases to smell of Cl, add  $\text{H}_2\text{SO}_4$  drop by drop, until the liquid after being warmed for a short time smells of  $\text{SO}_2$ ; then heat it short of boiling until the smell of  $\text{SO}_2$  is removed, and pour, through a filter if necessary, into the H apparatus. Great care must be taken to remove the  $\text{SO}_2$  entirely, else Sb and As may remain as sulphides in the H apparatus.

*Note 7.*—A residue here will contain Au or Pt if they are present; if they are to be tested for refer to (473, 474).

*Note 8.*—The precipitation by  $\text{H}_2\text{S}$  in the general table will often show in what condition As or Sn were present (427); further distinctive tests may be tried on the original solution by (187-190) and (201-203).

### 436. TABLE III A.—IRON GROUP.

The precipitate produced by boiling, after addition of  $\text{AmCl}$  and of  $\text{AmHO}$  in excess, may contain  $\text{Al}_2\text{HO}_6$ ,  $\text{Cr}_2\text{HO}_6$ ,  $\text{Fe}_2\text{HO}_6$ ; the color of the precipitate will usually show whether it contains any quantity of  $\text{Fe}_2\text{HO}_6$  (reddish-brown), or  $\text{Cr}_2\text{HO}_6$  (pale green), since  $\text{Al}_2\text{HO}_6$  is colorless.

Dissolve the precipitate by pouring upon the filter a little boiling dilute  $\text{HCl}$ , add to the solution pure  $\text{KHO}$  or  $\text{NaHO}$  until the precipitate remains after stirring, then add  $\text{KHO}$  or  $\text{NaHO}$  in considerable excess, boil for some time and filter:

1. *Filtrate* may contain  $\text{Al}_2\text{HO}_6$  dissolved in excess of  $\text{NaHO}$ ; if it is green,  $\text{Cr}_2\text{HO}_6$  is also in solution and must be precipitated by further boiling in a porcelain dish and then removed by filtration.

Add strong  $\text{HCl}$  gradually to the liquid drop by drop; a colorless gelatinous precipitate will form, should Al be present. If acid is added in excess this precipitate dissolves, but reappears on adding  $\text{AmHO}$  in excess. The appearance of this precipitate shows:

*Presence of Al.*

*Note.*—Sodium and potassium hydrates are very liable to contain  $\text{Al}_2\text{HO}_6$ ; the analyst must ascertain that the Al does not come from this source.

2. *Precipitate* may contain  $\text{Cr}_2\text{HO}_6$  and  $\text{Fe}_2\text{HO}_6$ . Dry upon the filter, carefully avoiding charring the paper; when sufficiently dried the substance will have shrunk considerably into small, hard, dark-colored pieces; detach these from the filter and fuse them with a little solid  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  upon a piece of platinum foil, either supported upon a pipeclay triangle or held in the Bunsen flame by crucible-tongs. Continue the fusion by heating the under surface of the foil in the blowpipe flame as long as any frothing occurs, then allow to cool; a yellow mass indicates the presence of Cr (Note 1). Boil the platinum foil in a small porcelain dish with water until the substance is entirely dissolved or only a dark-brown powder ( $\text{Fe}_2\text{O}_3$ ) remains undissolved; take out the foil, allow the powder to settle, and decant the liquid through a filter:

3. *Filtrate* will be yellow if Cr is present (Note 1 a). Add  $\text{HA}$  gradually until it is in excess, which is shown by the color becoming reddish, boil for several minutes, then add  $\text{PbAc}_2$  solution; a yellow precipitate shows:

*Presence of Cr (Note 2).*

4. *Residue* in porcelain dish; dissolve by pouring in a little  $\text{HCl}$  and boiling, add some water, then a few drops of  $\text{KCys}$  solution; a blood-red coloration shows:

*Presence of Fe (Note 3).*

*Note 1.*—If Mn was present in the original substance, it is often precipitated more or less completely with the Fe, and will be detected by imparting to the fused mass a bluish-green color; this should be noted, as the Mn may possibly be entirely precipitated in this group, and will then not be detected in the next group.

*Note 1 a.*—The green color, due to the presence of Mn, conceals the pale-yellow color due to Cr; but on dissolving the cool mass in water and boiling with H<sub>2</sub>A, the manganese coloration is destroyed; and, on filtering from any dark-colored precipitate, the yellow color due to Cr becomes evident.

*Note 2.*—Cr may have been present as a chromic salt, Cr replacing H in an acid; or as a chromate, Cr being united with O to form an acid-radicle. Ascertain in which state it was present by boiling some of the original substance with Na<sub>2</sub>CO<sub>3</sub> solution and filtering; a yellow filtrate, which on being acidified with H<sub>2</sub>A gives a yellow precipitate with PbA<sub>2</sub>, shows that Cr was *present as a chromate*; Cr, previously combined with an acid as a chromic salt, remains undissolved as green Cr<sub>2</sub>H<sub>2</sub>O<sub>6</sub>, and does not color the filtrate: it is found by 2 in the above table.

*Note 3.*—Fe is always detected here in the ferric condition, since, even if originally present as ferrosium, it will have been oxidized by boiling with HNO<sub>3</sub> as directed in the general table. To ascertain in which condition the Fe was present, boil some of the original substance with HCl, and divide the HCl solution, after filtering, if necessary, into two parts: to one portion add K<sub>6</sub>Fe<sub>2</sub>Cy<sub>12</sub>, a dark-blue precipitate shows *presence of Fe'' (Ferrosium)*; to another portion add KCyS, a blood-red color shows *presence of Fe''' (Ferricum)*.

### 437. TABLE III B.—ZINC GROUP.

The precipitate produced by Am<sub>2</sub>S in the solution or in the filtrate from Group III A, may contain ZnS, MnS, NiS, CoS. The color of the precipitate will usually show whether it contains any quantity of NiS or CoS which are black, or consists only of MnS (pink) or ZnS (white).

The presence of Ni, indicated by the filtrate after boiling with AmHO in the general table being blue in color, and also by a dark-brown filtrate being obtained after boiling with Am<sub>2</sub>S, will usually have been proved to a certainty by the examination in the borax bead of the black NiS, precipitated by boiling the dark-brown filtrate from Am<sub>2</sub>S (431); if Ni has been thus found its further detection in the Am<sub>2</sub>S precipitate, as directed below, will be unnecessary.



Remove the precipitate from the filter with cold dilute HCl in the liquid to stand, occasionally stirring it well. The precipitate milky liquid may be at once examined by 2 (below), or a black (below), the filtrate being examined by 2:

1. *Residue* (black) may contain NiS, CoS.

*Examination by the borax bead:*

Fuse a small quantity in a clear borax bead in the extreme tip of the outer blowpipe flame, note its color; then fuse the bead for some time in the inner blowpipe flame, and again observe its color. Any one of the following observations may be made:

*Blue bead* in both flames shows:

*Presence of Co.*  
Co need not be further tested for, but if any doubt exists as to the presence of Ni the rest of the residue must be examined as below.

*Brown or yellow bead*, when cold after fusing it in the outer flame, which becomes *gray or opaque*, in the inner flame, shows *presence of Ni, absence of Co.*

Unless mere traces of Co have to be tested for, no further examination need be made.

*A bead which is neither brown nor blue*, but of some intermediate hue on cooling from the outer flame, indicates the probable presence of both Co and Ni.

Examine the remainder of the black residue as directed below for Ni and Co, or for Co alone if Ni has been already detected by (431).

*Further Examination of the Residue.*—Rinse the residue from the filter into a porcelain dish, using as little water as possible; pour in a little strong HCl and boil for some time, adding occasionally a small crystal of  $\text{KClO}_3$ , until the black residue is entirely dissolved or only a small quantity of dark sulphur remains; then boil down nearly to dryness, a blue liquid shows *presence of Co*; dilute with a little water, filter if necessary into a boiling-tube and pour in KCy solution slowly until the precipitate formed at first is just redissolved; boil briskly for several minutes, and add much strong  $\text{Na}_2\text{H}_2\text{O}$ , or make decidedly alkaline with NaOH and add much Br-water; heat nearly to boiling, and allow the liquid to stand at least ten minutes, filter (Note 1, page 257):

3. *Precipitate* (black): wash and confirm the presence of Ni by fusing some of the precipitate, or the paper stained with the precipitate, in a borax bead in the outer and inner blowpipe flames; a bead *yellow* when cold, becoming *black* in the inner flame shows:

*Presence of Ni.*

4. *Filtrate* must be warmed with more  $\text{Na}_2\text{Cl}_2\text{O}$  or Br-water, and filtered from any additional precipitate which may form, then evaporated to dryness and strong  $\text{HNO}_3$  poured upon the residue as long as any frothing is caused; this is then evaporated just to dryness, the residue dissolved in water, excess of KHO added to it, and any precipitate filtered off and fused into a borax bead, taking the paper stained by the precipitate; if the precipitate is not easily removed, a blue bead shows:

*Presence of Co.*

## 438. TABLE IV.—BARIUM GROUP.

The precipitate produced by  $\text{Am}_2\text{CO}_3$  may contain  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ; it is to be well washed with boiling water. Before dissolving the precipitate off the filter much may usually be learnt by an examination of the flame coloration yielded by the HCl solution (see 1 below). The results thus obtained are afterwards confirmed in the wet way (see 2 below).



the way described in par. 26 c; take out the paper and allow it to either dissolve, leaving only white sulphur, in which case the residue will be left which must be filtered off and examined by 1

*Solution or filtrate may contain Zn, Mn.*

Boil in a porcelain dish until it ceases to smell of  $\text{H}_2\text{S}$ , then drop in a small crystal of  $\text{KClO}_3$  and boil for several minutes. After cooling the liquid add pure  $\text{NaHO}$  until after stirring the liquid it turns red litmus-paper blue, then add more  $\text{NaHO}$ , stir well and filter:

*Precipitate is white at first, but rapidly darkens in the air. Fuse a portion of it with solid  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  on platinum foil; a bluish-green mass is obtained on cooling showing:*

*Presence of Mn.*

*Note.*— $\text{Mn}$  may have been originally present either replacing  $\text{H}$  in an acid, or combined with  $\text{O}$  as an acid-radicle. Its presence in an acid-radicle is indicated by the color of the original solution, since in the form of manganate it is green, and as permanganate it is purple; these colors disappear on boiling the  $\text{HCl}$  solution for some time, or on passing  $\text{H}_2\text{S}$ .

6. *Filtrate:* pass  $\text{H}_2\text{S}$ , a white precipitate forms, often somewhat discolored, showing:

*Presence of Zn.*

*Note.*—From a dilute solution of  $\text{ZnHO}_2$  in  $\text{NaHO}$  the  $\text{ZnHO}_2$  is precipitated on boiling; hence after adding  $\text{NaHO}$ , as directed above, the liquid must not be boiled, else  $\text{Zn}$  might be precipitated with the  $\text{MnHO}_2$  and escape detection.

But by diluting and boiling the above filtrate it is usually possible to cause any  $\text{ZnHO}_2$  it holds in solution to precipitate, especially if the alkalinity of the liquid be somewhat reduced by cautious addition of  $\text{HCl}$  in quantity insufficient to make the liquid acid. If this precipitate be separated by pouring the liquid through a double filter and then be dissolved off the filter and the sides of the boiling-tube by a little boiling  $\text{HA}$ ,  $\text{ZnS}$  may be precipitated perfectly white from this solution by  $\text{H}_2\text{S}$ , showing:

*Presence of Zn.*

*Note 1.*—If this precipitate adheres to the sides of the boiling-tube, it is dissolved, after the liquid has been emptied out, by pouring in a little boiling  $\text{HCl}$ ; from this solution the  $\text{Ni}$  is precipitated by addition of  $\text{KHO}$ , and the precipitate filtered off and tested by the borax bead for  $\text{Ni}$ .

1. *Examination by Flame Coloration.*—Take a small quantity of the precipitate off the filter upon the end of a glass rod, and dissolve it by moving the end of the rod about in several drops of  $\text{HCl}$  on a watch-glass; dip into this solution a loop of platinum wire which imparts no color to the flame, then hold the loop for some time in the Bunsen flame, repeating the process if the coloration is not satisfactorily observed at first.  $\text{Ca}$  will impart to the flame a yellowish-red color,  $\text{Sr}$  a crimson-red,  $\text{Ba}$  a yellowish-green. The red colorations yielded by  $\text{Ca}$  and  $\text{Sr}$  are distinguished by viewing the flame through the

indigo-prism; the Ca coloration then appears *dingy green*, whilst its coloration remaining after the others have disappeared. When interfere with one another; but if at any time a red color is visible without using the prism, the presence of Ba

2. *Examination in the Wet Way.*—The rest of the precipitate again boiling the liquid, and pouring it once more through the the solution is acid, and if it is not, add H<sub>2</sub>A whilst stirring acid solution into a test-tube, and put by the larger portion (B). lower part of the tube in cold water or holding it in a stream from precipitate forms refer to Column I (below); if no immediate then forms refer to Column II; if no precipitate forms even

<p>I. An immediate precipitate is produced by CaSO<sub>4</sub> in the cold, showing:  <i>Presence of Ba.</i></p> <p>Portion (B) must then be tested for Sr and Ca which may also be present; examine it as directed below:</p> <p>Add K<sub>2</sub>CrO<sub>4</sub> solution until the color of the liquid is reddish-yellow; heat, and filter through a double filter-paper, pouring the filtrate through the same filter repeatedly if necessary until the liquid is quite clear; then add to the liquid, which must be orange-red in color, AmHIO until the color changes to pale yellow, then add Am<sub>2</sub>CO<sub>3</sub> solution:</p>		
<p>No precipitate forms, showing:  <i>Absence of Sr and Ca.</i></p>	<p>A precipitate forms, showing Sr, Ca, or both of them, to be present. Add to the liquid Am<sub>2</sub>CO<sub>3</sub> in excess, filter, reject the filtrate and dissolve the precipitate off the filter in as little boiling H<sub>2</sub>A as possible; pour off a small part (A') of this solution, reserving the larger portion (B'). To (A') add CaSO<sub>4</sub> solution and boil:</p>	
	<table> <tr> <td> <p>No precipitate forms:  <i>Absence of Sr.</i></p> <p>Examine portion (B') for Ca as directed at (C) in Column III.</p> </td><td> <p>A precipitate forms:  <i>Presence of Sr.</i></p> <p>Examine portion (B') for Ca as directed at (C), Column II.</p> </td></tr> </table>	<p>No precipitate forms:  <i>Absence of Sr.</i></p> <p>Examine portion (B') for Ca as directed at (C) in Column III.</p>
<p>No precipitate forms:  <i>Absence of Sr.</i></p> <p>Examine portion (B') for Ca as directed at (C) in Column III.</p>	<p>A precipitate forms:  <i>Presence of Sr.</i></p> <p>Examine portion (B') for Ca as directed at (C), Column II.</p>	

#### 439. TABLE V.—

The filtrate, after addition to the original solution of all the NH<sub>4</sub>. Since, however, NH<sub>4</sub>-salts have been added as group re-detected by boiling a portion of the original substance with KHO would be recognized by its smell or its action on moistened red NH<sub>4</sub>, since it will have been already tested for in the preliminary

the Sr coloration still appears *crimson*; Ba is usually found by all three metals are present together their colorations are apt to be through the indigo-prism, Sr is certainly present; if a green is proved.

is dissolved off the filter by pouring upon it a little boiling H<sub>2</sub>A, filter if the precipitate is not entirely dissolved. Test whether until the liquid is acid, then pour off a small portion (A) of the To the portion (A), after it has been cooled by immersing the the tap, add several drops of CaSO<sub>4</sub> solution; if an immediate precipitate forms heat the liquid to boiling, and if a precipitate after several minutes refer to Column III.

II. A precipitate is not formed at once on the addition of CaSO<sub>4</sub>, but appears on boiling the liquid, showing:

*Absence of Ba and presence of Sr.*

C. Portion (B) is then examined for Ca as directed below:

Add dilute H<sub>2</sub>SO<sub>4</sub> in excess, boil and filter, reject the precipitate; add to the filtrate several drops more H<sub>2</sub>SO<sub>4</sub> and boil; if this causes any precipitate boil and filter, and again test the filtrate by addition of H<sub>2</sub>SO<sub>4</sub> and boiling; repeat this process if necessary. To the clear filtrate, which gives no further precipitate on addition of H<sub>2</sub>SO<sub>4</sub> and boiling, add gradually AmHO until after mixing the liquid by thorough stirring or shaking, it turns red litmus-paper blue, then add Am<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution and warm gently; a white precipitate, often appearing only after a time, shows:

*Presence of Ca.*

(See note, Column III.)

III. No precipitate is produced by CaSO<sub>4</sub> even on boiling, showing:

*Absence of Ba and Sr, and presence of Ca.*

C. Confirm the presence of Ca by making portion (B) alkaline with AmHO (35 a), then add Am<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution; a white precipitate forms, showing:

*Presence of Ca.*

(See note below.)

*Note.*—If mere traces of Ca have to be tested for, the filter-paper used in the analysis must first be freed from any traces of Ca it may contain by wetting it with dilute HCl, and then thoroughly washing it with distilled water, as described in the note to par. 23 a (p. 63).

## POTASSIUM GROUP.

group reagents in succession, may still contain Mg, K, Na, and agents, it is useless to test for NH<sub>4</sub> in this filtrate; NH<sub>4</sub> must be solution, and ascertaining whether any NH<sub>3</sub> gas is evolved, which litmus-paper. It is, however, usually unnecessary to test here for examination (390). Proceed to examine for Group V as di-

rected below. Evaporate the filtrate from Group IV to dryness in a porcelain dish, scrape out the solid residue and heat it to redness upon a piece of platinum foil in the Bunsen flame as long as any white fumes are seen to be given off on removing the foil for an instant from the flame (Note 1). All  $\text{NH}_4$  compounds are thus entirely removed. If any residue remains (Note 2) it is to be dissolved by boiling the foil in a test-tube with a small quantity of water to which several drops of dilute  $\text{HCl}$  have been added. Divide this solution into two equal parts:

#### EXAMINATION FOR Mg.

Before testing for Mg in one portion of this solution it is necessary to remove from it any traces of Ba, Sr, or Ca which it may possibly contain,<sup>1</sup> and which might else be mistaken for Mg.

Add, therefore, several drops of  $\text{H}_2\text{SO}_4$  to the liquid, boil for a short time and let stand; then, whether a precipitate has formed or not, add a little  $\text{AmCl}$ , then  $\text{AmHO}$  in excess, then several drops of  $\text{Am}_2\text{C}_2\text{O}_4$ , and warm gently; if any precipitate has formed proceed to filter at once as quickly as possible. To the liquid in which the addition of  $\text{H}_2\text{SO}_4$ ,  $\text{AmCl}$ ,  $\text{AmHO}$  in excess, and  $\text{Am}_2\text{C}_2\text{O}_4$  causes no further precipitate add  $\text{Na}_2\text{HPO}_4$ , and if no precipitate forms at once warm gently, shake or stir the liquid violently and let it stand for some time; a white crystalline precipitate shows:

*Presence of Mg.*

#### EXAMINATION FOR K AND Na.

In the other portion proceed to test for K and Na as directed below. The presence of Mg in no way interferes with the detection of K and Na, and hence if it has been detected its removal is unnecessary.

*Flame Coloration.*—Dip into the solution a loop of platinum wire which has been proved when held in a Bunsen flame not to impart any color to it. Hold the loop in the Bunsen flame; one of the following results will be observed:

*A bright-yellow flame coloration, indicating the presence of Na (Note 3).*

Examine this coloration through the indigo-prism; it appears red, indicating *presence of K*; if no red color is visible K is probably absent or present only in very minute quantity.

*A pale-violet coloration, appearing crimson-red through the indigo-prism, shows: Presence of K, and absence of Na.*

It is usual to confirm the results of the examination of the flame coloration by pouring the remainder of the solution upon a watch-glass, adding to it several drops of  $\text{PtCl}_4$  (Note 4) and stirring well for some time; the formation of a yellow precipitate shows:

*Presence of K.*

See "Remarks (47)," and Note 5, page 261.

*Note 1.*—If the residue is small in amount it may be ignited in the dish; but this is not to be generally recommended, as the porcelain dish is liable to be cracked by the heat, and it is also difficult to get entirely rid of the  $\text{NH}_4$  salts by heating only in porcelain.

<sup>1</sup> Traces of Ba, Sr, Ca may remain unprecipitated by  $\text{Am}_2\text{CO}_3$  in Group IV.

*Note 2.*—It is not safe to place much reliance upon an examination of the foil for the detection of a small quantity of residue, but it may usually be detected by its producing a crackling noise whilst the foil is cooling immediately after its removal from the flame. Should there be any doubt, the foil must be boiled with water and a drop of  $\text{HCl}$ , and the solution examined for  $\text{Mg}$ ,  $\text{K}$ , and  $\text{Na}$ , as directed above.

*Note 3.*—A yellow coloration, more or less intense, will almost always be obtained here, since nearly all substances and reagents contain small quantities of  $\text{Na}$ ; hence the student must note the intensity of the coloration, and judge from it whether the quantity of  $\text{Na}$  is small or large; he must then enter accordingly, either "*Presence of Na*," or "*Presence of trace of Na*."

*Note 4.*—If iodine is present,  $\text{PtCl}_4$  will produce an intense red coloration; hence if iodine is suspected to be present, before adding  $\text{PtCl}_4$  the above solution should be evaporated to dryness with a little strong  $\text{HNO}_3$ , the residue dissolved in a few drops of dilute  $\text{HCl}$  and tested with  $\text{PtCl}_4$  for  $\text{K}$ . This is of course unnecessary if, before precipitating Group III in the general table, the solution has been evaporated to dryness with  $\text{HNO}_3$ . In case of uncertainty, add  $\text{PtCl}_4$  to a drop only of the above solution; and if iodine is found to be present proceed as directed above.

*Note 5.*—Mere traces of  $\text{K}$  and  $\text{Na}$  may be detected by adding  $\text{PtCl}_4$ , and evaporating the liquid to dryness in a porcelain dish upon a water-bath (504); then pouring absolute alcohol into the dish and stirring; any yellow residue shows *presence of K*, the solution giving the pure  $\text{Na}$  coloration if  $\text{Na}$  is present. By filtering off the yellow residue and washing it with absolute alcohol, it will yield the pure  $\text{K}$  flame coloration.

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## EXAMINATION FOR ACID-RADICLES.

**440.** Several acid-radicles will probably have been already detected for certain, if present, by the preliminary examinations. Such are  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{S}$ ,  $\text{NO}_2$ ,  $\text{ClO}$ ,  $\text{NO}_3$ ,  $\text{ClO}_2$ ,  $\text{A}$ : their reactions are so characteristic, that unless interfered with by the presence of other substances, their presence or absence will have been proved to a certainty: in case any uncertainty is felt, the analyst should refer to the reactions given in Section IV for the particular acid-radicle in question and select a reaction which will be decisive.

The examination for metals also frequently yields proof of the presence of certain acid-radicles. Thus on passing  $\text{H}_2\text{S}$  into the  $\text{HCl}$  solution:



- A reddish-yellow solution, becoming green and depositing white sulphur, shows . . . . . *Presence of  $CrO_4$*
- A green solution, becoming colorless, shows . . . . . *Presence of  $(MnO_4)''$*
- A purple solution, becoming colorless, shows . . . . . *Presence of  $(MnO_4)'$*
- A yellow precipitate of  $As_2S_3$ , appearing only when the liquid is boiled, shows . . . . . *Presence of  $AsO_4$*
- An insoluble residue of  $SiO_2$ , after evaporating to dryness the filtrate from the  $H_2S$ -group, shows . . . . . *Presence of  $SiO_3$*
- And a yellow precipitate obtained with  $AmHMoO_4$  before precipitating Group III, shows . . . . . *Presence of  $PO_4$*

The presence of any of these acid-radicles thus detected will require no further confirmation.

441. Of the acid-radicles which remain to be tested for, some can be detected by the plan drawn out below (442-445); others are best detected by special tests made on the original substance (446-454).

Much time and trouble may usually be saved by considering what acid-radicles can possibly be present. A careful preliminary examination will usually have limited this number considerably, and it may be further reduced

443.	I. Portion acidified with $HCl$ .	Present.
	On addition of $BaCl_2$ solution a white precipitate insoluble on boiling (444, 1), . . . . .	$(SO_4)''$
	On addition of $BaCl_2$ solution, a semi-transparent precipitate insoluble on boiling (444, 2), . . . . .	$(SiF_6)''$
	On addition of $AmCl$ and $Am_2CO_3$ , a semi-transparent precipitate, . . . . .	$(SiO_2)''$
	On addition of $FeSO_4$ solution, a dark-blue precipitate, . . . . .	$(Fe_2Cy_{12})^{vi}$
	On addition of $Fe_2Cl_6$ solution, a dark-blue precipitate: } $FeSO_4$ yielding a light-blue precipitate, . . . . .	$(FeCy_6)^{iv}$
	On addition of $Fe_2Cl_6$ solution, a red coloration destroyed by pouring into $HgCl_2$ solution, . . . . .	$(CyS)'$

<sup>1</sup> F will be readily detected in this precipitate, or better

by the knowledge already obtained as to the solubility of the substance under analysis, and the metals it contains. A reference to the table of solubilities (455), and the explanatory paragraphs 456, 457, and 458 will show how this knowledge is applied.

### GENERAL EXAMINATION FOR CERTAIN ACID-RADICLES.

**442.** Before employing the liquid tests it is advisable to separate from the substance any metals other than K, Na, and NH<sub>4</sub>, which it may contain, since some of these are liable to be precipitated by the reagents added for the detection of the acid-radicles. If alkali-metals alone are present this separation is unnecessary, since they are not precipitated by any of the reagents.

This separation of the metals may usually be effected by boiling a portion of the substance with Na<sub>2</sub>CO<sub>3</sub> solution, which must be added as long as it causes any precipitate. Filter from the precipitate, and divide the clear filtrate into five equal portions. Reserve one of these portions in case of accident and a second for the tests for organic acid-radicles, and acidify the others whilst they are hot by addition of HCl, HNO<sub>3</sub>, and H<sub>2</sub>A respectively: examine these portions as directed below, using a separate part for each test:

II. Portion acidified with HNO <sub>3</sub> . Refer to (444, 3).	Present.	III. Portion acidified with H <sub>2</sub> A.	Present.
On addition of AgNO <sub>3</sub> , a pure white precipi- tate, easily soluble in AmHO (444, 1), . . . }	Cl'	On addition of PbA <sub>2</sub> } solution a yellow pre- cipitate, . . . }	(CrO <sub>4</sub> )''
On addition of AgNO <sub>3</sub> , a light-yellow precipi- tate, with difficulty sol- uble in AmHO, . . . }	Br'	On addition of CaCl <sub>2</sub> so- lution a white gelat- inous precipitate, . . . }	F', <sup>1</sup> probably.
On addition of AgNO <sub>3</sub> , a yellow precipitate, almost insoluble in AmHO, . . . }	I'	On addition of CaCl <sub>2</sub> a white pulverulent pre- cipitate, . . . }	(C <sub>2</sub> O <sub>4</sub> )'', <sup>1</sup> probably.
Refer to (445).		On addition of Fe <sub>2</sub> Cl <sub>3</sub> a yellowish-white pre- cipitate (449, 450), . . . }	(PO <sub>4</sub> )''', or (AsO <sub>4</sub> )'''.

in the original substance by (452), (C<sub>2</sub>O)'' by (453).

## NOTES ON THE PRECEDING TABLE.

**444.** 1. Unless the  $\text{Na}_2\text{CO}_3$  solution used in preparing the solution for these tests was pure,  $(\text{SO}_4)''$  and  $(\text{Cl})'$ , if detected, may have been present only as impurities in the  $\text{Na}_2\text{CO}_3$ ; portions of the original substance should then be tested by (446) and (447).

2. The presence of  $(\text{SiF}_6)''$  should be confirmed by other tests, such as adding  $\text{KCl}$  (300), or evolving  $\text{HIF}$  by strong  $\text{H}_2\text{SO}_4$  (301); the  $\text{HIF}$  is most readily evolved from the  $\text{BaSiF}_6$  precipitate (301 a).

3. Should  $\text{AgNO}_3$  yield a black precipitate, this proves the presence of a sulphide, or possibly a thiosulphate; add  $\text{HNO}_3$ , and boil; the black  $\text{Ag}_2\text{S}$  will thus be decomposed, leaving a milky liquid, in which any other precipitate is readily seen after being coagulated by heating or shaking.

**445.** It must be remembered that  $(\text{Cy})'$ ,  $(\text{FeCy}_6)^{\text{iv}}$ ,  $(\text{Fe}_2(\text{Cy}_{12})^{\text{vi}}$ , and  $(\text{CyS})$  are also precipitated by  $\text{AgNO}_3$ , and therefore if these acid-radicles have been already found, a precipitate produced by  $\text{AgNO}_3$  does not prove the presence of  $(\text{Cl})'$ ,  $(\text{Br})'$ , or  $(\text{I})'$ , which acid-radicles must be specially examined for, as directed below.

If chloride, bromide, and iodide have all to be tested for, a portion of the  $\text{Na}_2\text{CO}_3$  solution must be examined by (273); or the precipitate obtained by  $\text{AgNO}_3$  (see 443, II) may be tested by (273 a) for  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ .

If only bromide and iodide have to be tested for, use par. 274.

## SPECIAL TESTS FOR ACID-RADICLES TO BE MADE ON THE ORIGINAL SUBSTANCE.

**446. Sulphate.**—A portion of the original substance is boiled with  $\text{HCl}$ , the liquid decanted or filtered if not clear, and  $\text{BaCl}_2$  added to it: a white precipitate shows *presence of  $\text{SO}_4$* .

**447. Chloride.**—A portion of the original substance is warmed with  $\text{HNO}_3$ , the solution decanted or filtered if necessary, and  $\text{AgNO}_3$  solution added to it, a *perfectly white* precipitate, easily dissolved by warm  $\text{AmHO}$ , shows *presence of chloride*.

**448. Cyanide** if present will have been detected by its special test and by the smell of bitter almonds, which is given off by the substance, after adding  $\text{H}_2\text{SO}_4$  (411). Add to some of the substance  $\text{Am}_2\text{S}$  in excess and boil; filter from any dark-colored precipitate, boil the filtrate for a short time, acidify with  $\text{HCl}$  and add  $\text{Fe}_2\text{Cl}_6$ ; a red coloration, not destroyed by heat but removed by addition to  $\text{HgCl}_2$ , shows *presence of  $\text{Cy}$* , possibly as  $(\text{FeCy}_6)^{\text{iv}}$ ,

( $\text{Fe}_2\text{Cy}_{12}$ )<sup>vi</sup>, or ( $\text{CyS}$ ), if these acid-radicles have been found (443, 1).

449. *Arsenate*.—This acid-radicle cannot be present unless As was detected during the examination for metals; the presence of  $(\text{AsO}_4)'''$  is there rendered probable by the precipitation of yellow  $\text{As}_2\text{S}_3$  occurring only when the liquid saturated with  $\text{H}_2\text{S}$  is boiled. If As has been found amongst the metals, proceed to test for  $(\text{AsO}_4)'''$  by adding to a portion of the  $\text{Na}_2\text{CO}_3$  solution (442)  $\text{HCl}$  until it is acid, then  $\text{AmCl}$ ,  $\text{AmHO}$  in excess, and  $\text{MgSO}_4$ ; filter off any precipitate which forms on warming and shaking the liquid, and pour a few drops of  $\text{AgNO}_3$  solution upon the white precipitate on the filter; a change of color to brown shows *presence of*  $(\text{AsO}_4)'''$ .

450. *Phosphate*.—Boil some of the original substance with dilute  $\text{HNO}_3$ , add a little of this clear solution, filtered if necessary, to some  $\text{AmHMoO}_4$  solution, shake and stir the liquid well, and if no precipitate forms warm *very gently*; a yellow precipitate shows *presence of*  $(\text{PO}_4)'''$ .

If  $(\text{AsO}_4)'''$  has been detected (449) this test for  $(\text{PO}_4)'''$  is only trustworthy when the yellow precipitate has been obtained either in the cold or by employing a *very gentle* heat. If any doubt is felt concerning the presence of  $(\text{PO}_4)'''$ , boil some of the substance with strong  $\text{HCl}$ , and examine for  $(\text{PO}_4)'''$  after having entirely separated the  $(\text{AsO}_4)'''$  by passing  $\text{H}_2\text{S}$  into the boiling  $\text{HCl}$  solution. A doubtful precipitate with  $\text{AmHMoO}_4$  may be proved to contain phosphate by dissolving it in  $\text{AmHO}$ , adding  $\text{AmCl}$  and  $\text{MgSO}_4$ , filtering and dropping  $\text{AgNO}_3$  upon the precipitate; if phosphate is present it turns *yellow*, if arsenate *brown*.

451. *Borate*.—Warm a portion of the substance with a little dilute  $\text{HCl}$ , dip into the solution a strip of turmeric-paper and dry it in a steam-oven or at a gentle heat; if the slip is *reddish-brown* and becomes *blue-black* when moistened with  $\text{AmHO}$ , the *presence of*  $(\text{BO}_3)'''$  is shown.

452. *Fluoride*.—Pour upon a portion of the powdered substance strong  $\text{H}_2\text{SO}_4$ ; and warm the mixture in a leaden or platinum crucible covered with a watch-glass, which has been coated with wax or paraffin, and has then had characters traced through the film with the point of a penknife: the characters are etched upon the glass, showing *the presence of F*.

If  $\text{SiO}_2$  is known to be present, the test must be made by conducting the gas, evolved on heating the substance with strong  $\text{H}_2\text{SO}_4$ , into dilute  $\text{AmHO}$ , when a deposit of gelatinous  $\text{H}_4\text{SiO}_4$  proves the presence of *F*.

**453. Oxalate.**—The precipitate produced by  $\text{CaCl}_2$  in III (443), or the original substance if it contains no carbonate, is mixed on a watch-glass with  $\text{MnO}_2$  free from carbonate, and strong  $\text{H}_2\text{SO}_4$ , and gently warmed:  $\text{CO}_2$  is evolved and detected by holding over the bubbles which rise from the mixture a rod moistened with lime-water, or by inverting another watch-glass containing on its under surface a drop of lime-water over the glass containing the mixture.

**453 a. Tartrate.**—The presence of *T* will probably have been indicated in the preliminary examination (388 or 412). In order to confirm its presence, any metals of Groups I, II, and III must be separated by  $\text{H}_2\text{S}$  or  $\text{Am}_2\text{S}$ , and  $\text{CaT}$  is then precipitated from the liquid, made just alkaline with  $\text{AmHO}$  and mixed with a little  $\text{AmCl}$ , by adding excess of  $\text{CaCl}_2$ , shaking well and letting stand for some time. A precipitate may consist of

#### 455. TABLE SHOWING THE SOLUBILITY OF

A blank signifies that the solubility

		<i>K.</i>	<i>Na.</i>	<i>Am.</i>	<i>Mg.</i>	<i>Ba.</i>	<i>Sr.</i>	<i>Ca.</i>	<i>Fe''.</i>	<i>Fe'''.</i>	<i>Al.</i>	<i>Cr.</i>	<i>Zn.</i>	<i>Mn.</i>	<i>Ni.</i>
1.	Oxide . .	w.	w.	w.	a.	w.	w.	w-a.	a.	a.	a.i.	a.i.	a.	a.	a.
2.	Sulphide .	w.	w.	w.	w-a.	w.	w.	w-a.	a <sup>m</sup> .	a.	—	—	a.	a.	a <sup>m</sup> .
3.	Chloride .	w.	w.	w.	w.	w.	w.	w.	w.	w.	w.	a.i.	w.	w.	w.
4.	Iodide . .	w.	w.	w.	w.	w.	w.	w.	w.	w.	—	—	w.	w.	—
5.	Sulphate .	w.	w.	w.	w.	i.	i.	w-a <sup>m</sup> -i.	w.	w.	w.	w-a.	w.	w.	w.
6.	Nitrate . .	w.	w.	w.	w.	w.	w.	w.	w.	w.	w.	w.	w.	w.	w.
7.	Phosphate	w.	w.	w.	a.	a.	a.	a.	a.	a.	a.	a.	a.	a.	a.
8.	Carbonate	w.	w.	w.	a.	a.	a.	a.	a.	—	—	—	a.	a.	a.
9.	Borate . .	w.	w.	w.	a.	a.	a.	a.	a.	a.	a.	a.	a.	a.	a.
10.	Arsenite .	w.	w.	w.	a.	a.	a.	a.	a.	a.	a.	a.	a.	a.	a.
11.	Arsenate .	w.	w.	w.	a.	a.	a.	a.	a.	a.	—	—	—	—	a.
12.	Chromate .	w.	w.	w.	w.	a.	a.	a.	—	w.	a.	a.	w.	i.	a.
13.	Fluoride .	w.	w.	w.	a.	a-i.	i.	a-i.	—	—	—	—	—	—	—
14.	Oxalate . .	w.	w.	w.	a.	a.	a.	a.	a.	a.	a.	w-a.	a.	w-a.	a.

Only the most commonly occurring compounds are contained in this table; the solubility of other substances may be obtained by reference to Storer's "Dictionary of Solubilities."

**456.** The table is thus arranged: in a horizontal line at the head



CaT,  $\text{Ca}_3(\text{PO}_4)_2$ , or CaO. By shaking this precipitate with cold KHO solution, CaT is dissolved and may be reprecipitated from the solution or filtrate by diluting and boiling for some time; the liquid is decanted and the precipitate is then gently warmed with a little *very dilute* AmHO and a crystal of  $\text{AgNO}_3$ ; a metallic mirror shows the *presence of T*.

**454. Sulphide.**—Very small quantities of S may be detected by boiling the substance with KHO for some time, and adding to the clear solution alkaline  $\text{PbA}_2$  solution, when a black precipitate or coloration will appear.

The above directions must only be considered as affording examples of how the principal acid-radicles are detected. By reference to the individual reactions in Section IV and to the directions there given for the detection of similar acid-radicles when occurring together, this method will serve for the detection of all the commonly occurring acid-radicles.

## SUBSTANCES IN WATER AND ACIDS.

is unknown or unimportant.

Co.	Hg''.	Pb.	Bi.	Cu.	Cd.	Sb.	Sn''.	Sn'''.	As'''.	Ag.	Hg'.		
a.	a.	a <sup>n</sup>	a.	a.	a.	a <sup>m</sup>	a.	a.f.	w.a <sup>m</sup>	a <sup>n</sup>	a <sup>n</sup>	O.	1.
a <sup>m</sup> .	a <sup>m</sup> .	a <sup>n</sup>	a <sup>n</sup>	a <sup>n</sup>	a.	a <sup>m</sup>	a <sup>m</sup>	a <sup>m</sup>	a <sup>n</sup>	a <sup>n</sup>	a <sup>n</sup>	S.	2.
w.	w.	w.i.	w.b.	w.	w.	w.b.	w.b.	w.	w.	i.	a.i.	Cl.	3.
—	a.	w.a <sup>m</sup>	—	—	w.	—	w.	w.	—	i.	a <sup>n</sup>	I.	4.
w.	w.b.	a.i.	w.b.	w.	w.	a.	w.	w.b.	—	w.a <sup>n</sup>	w.b.a <sup>n</sup>	SO <sub>4</sub> .	5.
w.	w.b.	w.	w.b.	w.	w.	—	—	w.	—	w.	w.b.	NO <sub>3</sub> .	6.
a.	a.	a <sup>n</sup>	—	a.	a.	—	a.	—	—	a <sup>n</sup>	a <sup>n</sup>	PO <sub>4</sub> .	7.
a.	a.	a <sup>n</sup>	a.	a.	a.	—	—	—	—	a <sup>n</sup>	a <sup>n</sup>	CO <sub>3</sub> .	8.
a.	—	a <sup>n</sup>	a.	a.	w.a.	—	a.	—	—	—	w.	BO <sub>3</sub> .	9.
a.	a.	a <sup>n</sup>	a.	a.	—	a.	—	—	—	a <sup>n</sup>	a <sup>n</sup>	AsO <sub>2</sub> .	10.
a.	a.	a <sup>n</sup>	—	a.	—	a.	—	—	—	a <sup>n</sup>	a <sup>n</sup>	AsO <sub>4</sub> .	11.
—	w.a.	a <sup>n</sup> i.	a.	w.	—	a.	—	—	—	a <sup>n</sup>	a <sup>n</sup>	CrO <sub>4</sub> .	12.
—	w.	a.	—	—	—	—	—	—	—	w.	—	F.	13.
a.	a.	a.	a.	a.	a.	a.	a.	w.	—	a.	a.	C <sub>2</sub> O <sub>4</sub> .	14.

are placed the more commonly occurring metals, which yield salts or basic oxides; in the vertical column on the left is a list of that portion of the names of the compounds thus formed, which corresponds to the acid-radicle; the same are also placed in chemical symbols in a

vertical column on the right. The solubility of a compound is denoted by letters:

- w. Signifies soluble in water.
- a. Soluble in acids; the term standing for HCl, HNO<sub>3</sub>, and aqua regia.
- am. Soluble in muriatic, or hydrochloric acid.
- an. Soluble in nitric acid.
- amn. Soluble in a mixture of muriatic and nitric acids, or aqua regia, but not in either separately.
- i. Insoluble in water and acids.
- w.a. Letters thus placed together with a stop between, signify that in different states the substance shows these different solubilities.
- w-a. Letters connected by a hyphen indicate that the substance is only slightly soluble in the first solvent, and may therefore partially fall under the class denoted by the second letter.
- w.b. Decomposed more or less by much water with formation of a basic salt which is insoluble in water but soluble in acid.

**457.** To find the solubility of any compound of one of the metals placed at the top of the table, glance down the vertical column which is headed by this element; the letter indicating the solubility of the compound will be found in a horizontal line with the acid-radicle portion of the name. Thus to find the solubility of zinc sulphate, it is only necessary to glance down the vertical column with Zn at its head: on a horizontal line with "sulphate" (SO<sub>4</sub>) stands the letter *w*, showing the zinc sulphate is soluble in water.

**458.** The way in which this table is used after ascertaining the solubility of a substance under analysis, and detecting the metals present in it, may be explained by an example. In a substance *which was entirely soluble in water*, the metals found were K, Ba, Ag. We glance down the columns headed by these three metals, and can thus see at once which acid-radicles may be present: all acid-radicles might be present combined with K since all its salts are soluble in water, but the presence of Ba in a substance soluble in water shows that SO<sub>4</sub>, PO<sub>4</sub>, CO<sub>3</sub>, BO<sub>3</sub>, AsO<sub>3</sub>, AsO<sub>4</sub>, CrO<sub>4</sub>, and F cannot be present, since these acid-radicles form compounds with Ba which are insoluble in water; Ag excludes in addition S, Cl, Br, and I; hence amongst the more commonly occurring acid-radicles only NO<sub>3</sub> need be tested for.

This example shows how much we may often simplify the examination for acid-radicles, when the metals present in a substance and also its solubility are known, by referring to the above table.

## REMARKS ON THE PRECIPITATION OF GROUP III.

459. In the general table (419) it is assumed that in the absence of  $(\text{PO}_4)'''$  the two Sub-groups III A and III B can be separated from one another by adding first  $\text{AmCl}$  and then excess of  $\text{AmHO}$  to the solution; Group III A alone being thus precipitated, and Group III B being afterwards precipitated by adding  $\text{Am}_2\text{S}$  to the filtrate. Now although  $\text{AmCl}$  entirely prevents the precipitation of Group III B by  $\text{AmHO}$ , if the solution is kept covered from the air, still if the members of Group III A are present at the same time in the solution they are precipitated by  $\text{AmHO}$ , and the presence of  $\text{AmCl}$  will not prevent Mn and Zn from being precipitated with them in smaller or larger quantity, Mn particularly showing a tendency to be precipitated with Fe, and Zn with Cr. Hence if either Mn or Zn, especially the former, be present in small quantity only, it may be entirely precipitated in Group III A: this is not a serious matter in the case of Mn, since it is readily detected in the ordinary examination of the precipitate by Table III A by yielding a *green* mass on fusion with  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$ ; but Zn may be entirely passed over, since if precipitated with  $\text{Cr}_2\text{HO}_6$  its presence would certainly not be detected in Table III A. The method of dissolving the precipitate several times in  $\text{HCl}$  and reprecipitating with  $\text{AmHO}$ , to some extent meets this difficulty; but it is preferable whenever a precipitate is produced on adding  $\text{AmCl}$  and  $\text{AmHO}$ , and traces of Mn, and more particularly of Zn, have to be tested for, to precipitate Groups III A and III B together by adding in succession  $\text{AmCl}$ ,  $\text{AmHO}$ , and  $\text{Am}_2\text{S}$ , and boiling. The precipitate is then examined by Table III c (464, 465) for Groups III A and III B, the filtrate being examined, as directed in the general table, for Groups IV and V. It must, however, be understood that if no precipitate is produced by  $\text{AmCl}$  and  $\text{AmHO}$ ,  $\text{Am}_2\text{S}$  may be added, and the precipitate, if any, examined by

Table III B, since in the absence of Group III A the members of Group III B are not precipitated by  $\text{AmHIO}$  in the presence of  $\text{AmCl}$ .

**460.** *The presence of  $(\text{PO}_4)'''$  in the  $\text{HCl}$  solution* which is to be examined for Groups III, IV, and V involves no special procedure if  $\text{AmHIO}$  added after  $\text{AmCl}$  produces no precipitate, since the phosphates of Groups III and IV and of Mg must be absent. If, however, on adding  $\text{AmCl}$  and  $\text{AmHIO}$  a precipitate is formed, the directions given at the head of Table III D (466) must be followed, and the precipitate must be examined by that table. The reason for this departure from the ordinary course of analysis is that, whereas Al, Cr, Ba, Sr, Ca, and Mg, if present as phosphates, are completely precipitated by  $\text{AmHIO}$ , the phosphates of Ni, Co, Mn, Zn, and Fe are only partially precipitated by  $\text{AmHIO}$ ; their metals are, however, entirely precipitated by  $\text{Am}_2\text{S}$ . The filtrate from  $\text{Am}_2\text{S}$  is then examined as directed in the general table for Groups IV and V.

The principle on which the method drawn out in Table III D is founded are:

1. The insolubility of the phosphates of Al, Fe, and Cr in  $\text{H}\bar{\text{A}}$  in the presence of an alkaline acetate, the other portions of the precipitate being soluble.

2. The separation of all the  $(\text{PO}_4)'''$  which is in the  $\text{H}\bar{\text{A}}$  solution combined with Ba, Sr, Ca, or Mg, by  $\text{Fe}_2\text{Cl}_6$  in an  $\text{H}\bar{\text{A}}$  solution.

The further separation of Al, Fe, and Cr phosphates is somewhat complicated by the fact that  $\text{AlPO}_4$  is only decomposed by fusion mixture when  $\text{SiO}_2$  is also present, and this  $\text{SiO}_2$  has to be removed after the fusion by methods which will be intelligible on reference to (290, -291).

**461.** The reason why, in obtaining the precipitate for Table III D, the precipitates produced by  $\text{AmHIO}$  and  $\text{Am}_2\text{S}$  are filtered and washed separately, is that phosphates of Fe, Zn, Mn, Ni, and Co are converted by  $\text{Am}_2\text{S}$  into sulphides, forming at the same time ammo-

nium phosphate which remains in solution, and this would precipitate Ba, Sr, Ca, Mg as phosphates from the solution, even if they were not originally present in that condition. Now this besides complicating the process of analysis, would also render it impossible to state whether Ba, Sr, Ca, and Mg were originally present as phosphates or not. Hence the phosphates of Groups III and IV and of Mg are first precipitated by  $\text{AmCl}$  and  $\text{AmHO}$ , then any members of Group III B and any remaining traces of phosphates of Group III are precipitated from the filtrate by  $\text{Am}_2\text{S}$ . The two precipitates are mixed and treated with  $\text{Am}_2\text{S}$ , which will dissolve away the  $(\text{PO}_4)'''$  from Fe, Zn, Mn, Ni, Co phosphates if present, leaving the other phosphates undecomposed; hence, if on filtering and testing the filtrate with  $\text{AmCl}$ ,  $\text{AmHO}$ , and  $\text{MgSO}_4$  a white crystalline precipitate is obtained, this indicates the presence of  $(\text{PO}_4)'''$ , and indirectly establishes the presence in the original precipitate of phosphate of some one or more of the metals Fe, Zn, Mn, Ni, Co.

462. Oxalates, borates, fluorides, and silicates of Ba, Sr, Ca, Mg would likewise be precipitated by  $\text{AmHO}$  in Group III A; but by the evaporation of the  $\text{HCl}$  solution after passing  $\text{H}_2\text{S}$ ,  $\text{H}_3\text{BO}_3$  and  $\text{HF}$  are usually volatilized, and  $\text{H}_2\text{SiO}_3$  becomes insoluble; oxalates are also decomposed by a gentle ignition after evaporation.

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\* \* The best course to be pursued in precipitating and examining Group III will be found in (463).



### 463. RULES FOR THE PRECIPITATION AND EXAMINATION OF GROUPS III A AND III B.

Refer to pars. 459-462 for the explanation of these rules.

The following rules may be laid down for precipitating and detecting members of Groups III A and III B in the HCl solution, a small portion of which has been tested for  $(PO_4)'''$  by  $AmHMoO_4$ :

I. *If the addition of AmHIO after AmCl causes no precipitate*, showing the absence of Al, Fe, Cr and of their phosphates, and of phosphates of Ba, Sr, Ca, and Mg,  $Am_2S$  is at once added, the liquid boiled, and the precipitate, if any, examined for members of Group III B by Table III B (437): this course is pursued whether  $(PO_4)'''$  is present or absent, since even if phosphate is present, metals of Groups III and IV and Mg are not present as phosphates.

II. *If the addition of AmHIO after AmCl causes a precipitate, showing the presence of Al, Fe, Cr, and  $(PO_4)'''$  is not present*, the plan of precipitation depends upon the object of the analysis.

If small quantities of Zn need not be tested for, the method given in the general table (419) may be followed.

If traces of Zn have to be tested for in the solution, add AmCl, then AmHIO and  $Am_2S$  in excess, boil, filter, and examine the precipitate by Table III  $c_1$  (464) or III  $c_2$  (465). The method described in Table III  $c_1$  gives trustworthy results, and is to be used for very careful analysis; the method in Table III  $c_2$  is, however, much more simple, and is sufficiently accurate for general use.

III. *If the addition of AmHIO after AmCl causes a precipitate, and  $(PO_4)'''$  is present*, the method of precipitation to be adopted will be found in par. 466, together with the table for the examination of the group precipitate.

# 464. TABLE III C<sub>1</sub>.—THE SEPARATION OF GROUPS III A AND III B BY BaCO<sub>3</sub>.

The precipitate may contain Fe, Al, Cr, Zn, Mn, Ni, Co. Rinse it off the filter into a porcelain dish, using as little water as possible, add some strong HCl and boil, adding at intervals a small crystal of KClO<sub>3</sub> until all is dissolved but a small quantity of yellow sulphur. Evaporate very nearly to dryness, dilute with a little water, and pour, through a filter if necessary, into a small flask. Cool, pour in a small quantity of BaCO<sub>3</sub> suspended in water, cork the flask tightly and shake well; repeat the addition of BaCO<sub>3</sub> and agitation until the precipitate is distinctly whitened by the excess of BaCO<sub>3</sub>; then shake well and allow the flask to stand by corked for at least fifteen minutes, occasionally shaking it vigorously. Let the precipitate subside, filter; wash the precipitate with a little cold water, allowing the washings to run through into the filtrate, then wash thoroughly, rejecting the washing-water:

1. *Precipitate* may contain Fe, Al, Cr, and BaCO<sub>3</sub>; dissolve it in as little boiling HCl as possible; remove Ba from the *boiling* solution by adding dilute H<sub>2</sub>SO<sub>4</sub> gradually, until after allowing the precipitate to settle, a few additional drops of acid cause no further precipitate (Note 1, below); filter, add pure NaHO in excess to the filtrate, boil and filter:

*Precipitate*: examine for Fe and Cr by column 2, Table III A (436).

*Filtrate*: examine for Al by column 1, Table III A (436).

*Note. 1.*—The separation of Ba may be neglected here, the precipitate being at once boiled with NaHO: in this case much white BaCO<sub>3</sub> will remain with the Fe<sub>2</sub>O<sub>3</sub> after fusion to separate Cr; it will however dissolve with the Fe and cause no complication.

2. *Filtrate* may contain Zn, Mn, Ni, Co, and BaCl<sub>2</sub>. Remove Ba by adding to the *boiling* liquid dilute H<sub>2</sub>SO<sub>4</sub> gradually, until the last few drops produce no further precipitate in the clear liquid from which the BaSO<sub>4</sub> has been allowed to settle; filter, add pure NaHO in excess to the *cold* filtrate, stir well and filter.

*Precipitate* may contain Mn, Ni, Co; rinse off the filter into a porcelain dish with as little water as possible, add some strong HCl and boil; evaporate nearly to dryness, add a little strong solution of NaA to the liquid, pass H<sub>2</sub>S to saturation, filter:

*Filtrate*: pass H<sub>2</sub>S, a white precipitate indicates: Presence of Zn.

*Precipitate*: examine for Ni and Co according to Table III B, column 1 (437).

*Filtrate*: add AmHO in excess; a flesh-colored precipitate shows: Presence of Mn.

465. TABLE III c<sub>2</sub>.—FOR EXAMINATION OF

Remove the precipitate produced by  $\text{AmCl}$ ,  $\text{AmHO}$ , and dish, pouring in dilute  $\text{HCl}$ , and gently stirring and shaking residue is left, filter (see Note 1):

<i>Residue</i> if black may contain $\text{NiS}$ and $\text{CoS}$ ; examine it as directed in Table III B, column 1 (437).	<i>Filtrate</i> may contain $\text{Al}$ , $\text{Fe}$ , $\text{Cr}$ , $\text{Zn}$ , $\text{Mn}$ . Carefully note its result of this observation, examine the liquid by column	
	<p style="text-align: center;"><i>I. The liquid is perfectly colorless : Absence of Cr.</i></p> Boil the liquid in the dish for a few minutes until it no longer smells of $\text{H}_2\text{S}$ , then add a small crystal $\text{KClO}_3$ and boil down to a small bulk; cool, add $\text{NaHO}$ in excess, stir well and filter :	
	<i>Precipitate</i> may contain $\text{Fe}$ , $\text{Mn}$ . Dry and fuse it on platinum foil with $\text{Na}_2\text{CO}_3$ and $\text{KNO}_3$ ; a blue-green mass shows :	<i>Filtrate</i> may contain $\text{Zn}$ , $\text{Al}$ . Divide into two equal parts (Note 2). Into one portion pass $\text{H}_2\text{S}$ ; a white precipitate forms at once :
	<p style="text-align: center;"><i>Presence of Mn.</i></p> Boil the foil in a porcelain dish with water for some time, and if any undissolved residue is left, decant the liquid, boil the residue with $\text{HCl}$ , and add $\text{KCys}$ ; a blood-red coloration shows : <i>Presence of Fe</i> (Note 3, 436).	<p style="text-align: center;"><i>Presence of Zn.</i></p> To the other portion add dilute $\text{HCl}$ gradually whilst stirring; if no precipitate forms, add $\text{HCl}$ in excess, then $\text{AmHO}$ in excess, and heat; a colorless flocculent precipitate : <i>Presence of Al.</i>

*Note 1.*—A mere milkiness, due to the separation of sulphur, shows the

*Note 2.*— $\text{Al}$  and  $\text{Zn}$  may also be detected without dividing the filtrate by a colorless flocculent precipitate shows *Presence of Al*: this is filtered off and

## GROUPS III A AND III B, WHEN MIXED.

$\text{Am}_2\text{S}$  from the filter by opening the filter out inside a porcelain the liquid: take out the filter-paper, stir well, and if any *black*

color, which is best seen by pouring it into a white porcelain dish, and according to the I or II.

II. *The liquid has a violet or bright-green color: Presence of Cr.*

Boil the liquid in the dish until  $\text{H}_2\text{S}$  is no longer smelt, drop in a small crystal of  $\text{KClO}_3$  and boil down nearly to dryness; dilute with a little water, pour into a small flask and add  $\text{BaCO}_3$  suspended in water gradually while constantly shaking the liquid until the excess of  $\text{BaCO}_3$  whitens the precipitate; cork the flask and allow it to stand for not less than fifteen minutes, occasionally shaking it well; filter, wash first with cold water, letting the washings run into the filtrate, then with boiling water, rejecting the washings:

*Precipitate* may contain Fe, Al, Cr; examine it by column I, Table III C, (464).

*Filtrate* may contain Zn, Mn; boil, and whilst boiling, add dilute  $\text{H}_2\text{SO}_4$  gradually until the last few drops cause no further precipitate, filter from  $\text{BaSO}_4$ ; cool, add pure  $\text{NaHO}$  in excess, stir well and filter:

*Precipitate*: dry and fuse with  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  on platinum foil; blue-green mass:  
*Presence of Mn.*

*Filtrate*: pass  $\text{H}_2\text{S}$ ; white precipitate:  
*Presence of Zn.*

absence of Ni and Co, and does not render filtration necessary.

adding to it  $\text{HCl}$  gradually until it becomes acid, then  $\text{AmHIO}$  until alkaline;  $\text{H}_2\text{S}$  passed into the filtrate; a white precipitate shows *Presence of Zn.*

TABLE III D.—FOR EXAMINATION

**466.** If  $(\text{PO}_4)'''$  is found in the  $\text{HCl}$  solution in the general tests, the precipitate forms on addition of  $\text{AmCl}$  and excess of  $\text{AmHO}$ , the liquid is filtered, and the precipitate is washed well with hot water. To the filtrate and the filtrate examined for Groups IV and V (419, 431). The filtrate is examined for  $(\text{PO}_4)'''$  by adding  $\text{MgSO}_4$ ; if this is present, the residue left after stirring with  $\text{Am}_2\text{S}$  may contain  $\text{Ba}$ ,  $\text{Sr}$ ,  $\text{Ca}$ ,  $\text{Cr}$  as hydrates. Remove it from the filter and heat it with a drop in several small crystals of  $\text{KClO}_3$ , and evaporate very nearly to dryness. The residue is dissolved in  $\text{HCl}$  and  $\text{NaA}$  (526. 84), as long as any precipitate is pro-

<i>Filtrate</i> : Add $\text{Fe}_2\text{Cl}_6$ (Note 2) drop by drop as long as a precipitate forms, and until the liquid, after being well stirred or shaken, remains reddish; addition of $\text{Fe}_2\text{Cl}_6$ in large excess must be carefully avoided. Warm gently for some time, filter whilst hot, and wash with hot water:		
<i>Filtrate</i> : Add $\text{AmCl}$ , $\text{AmHO}$ (Note 3), and $\text{Am}_2\text{S}$ : filter:		
<i>Filtrate</i> : Add $\text{Am}_2\text{CO}_3$ : filter:	<i>Precipitate</i> : examine by Table III c (464, 465) for $\text{Zn}$ , $\text{Mn}$ , $\text{Ni}$ , $\text{Co}$ , also for $\text{Al}$ and $\text{Cr}$ . Test a portion of the original solution, or the solution of the substance in $\text{HCl}$ , for $\text{Fe}''$ and $\text{Fe}'''$ by Note 3 (436).	
<i>Precipitate</i> may contain $\text{BaCO}_3$ , $\text{SrCO}_3$ , $\text{CaCO}_3$ . Examine this precipitate by Table IV (438). $\text{Ba}$ , $\text{Sr}$ , $\text{Ca}$ , if found in this precipitate, were present in the solution as phosphates.	<i>Filtrate</i> may contain $\text{Mg}$ ; add $\text{Na}_2\text{HPO}_4$ , warm and shake well; white crystalline precipitate: <i>Presence of Mg as phosphate.</i>	<i>Precipitate</i> containing $\text{FePO}_4$ may be neglected.

*Note 1.*—An insoluble residue here may contain  $\text{SrSO}_4$  and  $\text{BaSO}_4$ , and must originally as phosphates.

*Note 2.*—A few drops of  $\text{Fe}_2\text{Cl}_6$  may be added to a small part only of the filtrate at once for Groups III and IV and for  $\text{Mg}$ , without adding  $\text{Fe}_2\text{Cl}_6$ .

*Note 3.*—Since this filtrate has to be tested for Groups III A and III B, it is precipitated by Table III c, or by precipitating Groups III A and III B precipitates by Tables III A and III B (436, 437).

*Note 4.*—Since  $\text{CrPO}_4$  is rarely present, this precipitate may generally be dissolved in  $\text{HCl}$ , and is detected by acidifying with  $\text{HCl}$  and adding  $\text{AmHO}$  in excess, and is detected by dissolving in  $\text{HCl}$  and adding  $\text{KCN}$ .



## OF PHOSPHATES IN GROUP III.

table (419) after precipitating Groups I and II, and a precipitate containing the precipitate is gently heated, filtered quickly, and  $\text{Am}_2\text{S}$  is added in excess, and the solution boiled, then filtered, two precipitates yielded by  $\text{AmHO}$  and by  $\text{Am}_2\text{S}$  are transferred to and the residue on the filter is washed well. The filtrate should contain Fe, Zn, Mn, Ni, Co, one or more were present as phosphates. Mg as phosphates; Fe, Zn, Mn, Ni, Co as sulphides; and Al, dilute  $\text{HCl}$  in a porcelain dish. If this does not dissolve it, to dryness. Filter off S if necessary (Note 1); then add a solution. Heat gently, and filter while hot:

*Precipitate* may consist of  $\text{FePO}_4$ ,  $\text{AlPO}_4$ ,  $\text{CrPO}_4$  (Note 4). Dry the precipitate on the filter, and fuse it for a short time in a platinum crucible or on platinum foil with a mixture of finely powdered  $\text{SiO}_2$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{KNO}_3$ . When cold dissolve by boiling with a little distilled water, add  $\text{Am}_2\text{CO}_3$ ; allow to stand for a short time, stirring occasionally; let the precipitate subside, filter:

*Filtrate*: add  $\text{H}_2\text{A}$  until the solution is acid, boil for a short time, then add  $\text{PbA}_2$ ; yellow precipitate of  $\text{PbCrO}_4$ . Presence of Cr as phosphate.

*Note*.—A white precipitate on addition of  $\text{PbA}_2$  may be disregarded.

*Precipitate* may contain  $\text{H}_2\text{SiO}_4$ , Fe and Al as silicates, and  $\text{Fe}_2\text{H}_2\text{O}_6$ . Acidify with  $\text{HCl}$ , evaporate to dryness, and heat the dry residue gently. Warm with a few drops of strong  $\text{HCl}$ , add hot water, and filter:

*Filtrate*: add pure  $\text{NaHO}$  in excess, boil and filter:

*Filtrate*: acidify with  $\text{HCl}$ , and add  $\text{AmHO}$  in excess, boil: white, gelatinous precipitate: Presence of Al as phosphate.

*Precipitate* is brown  $\text{Fe}_2\text{H}_2\text{O}_6$ : dissolve by boiling with  $\text{HCl}$ , and add  $\text{KCys}$ : blood-red coloration: Presence of Fe as phosphate.

*Residue* is  $\text{SiO}_2$  and may be neglected.

be examined by the latter part of (428): Ba or Sr, if found here, were present filtrate and heated; if it causes no precipitate the other portion may be examined by adding  $\text{AmCl}$ ,  $\text{AmHO}$ , and  $\text{Am}_2\text{S}$  together and analyzed separately by  $\text{AmCl}$  and  $\text{AmHO}$ , and then  $\text{Am}_2\text{S}$ , and by examining the pre-tested by boiling with excess of  $\text{NaHO}$ , and filtering;  $\text{AlPO}_4$  will be in excess, which gives a gelatinous precipitate;  $\text{Fe}_2\text{H}_2\text{O}_6$  remains as a precipitate,

### 467. ANALYSIS OF METALS AND ALLOYS.

After making the preliminary examination given below either of the two methods (470 or 471) may be adopted. The first method is by far the most ready and certain for the examination of a metal or alloy of unknown composition, since all metals, even when present in small quantity only, may thus be detected.

In making the solution by the second method, Sn, Sb, Au, and Pt are left undissolved, all other metals passing into solution; it is not, however, to be recommended as a *general* process for examination of metals and alloys, since the following complications are apt to occur. If As is present with Sn, a part or the whole of the As may remain in the residue; Pt, if present with a sufficient quantity of Ag, may pass entirely into solution; and Sb will always partly dissolve. The process, however, is useful in cases where an alloy, known to contain a large proportion of Sn or Sb, has to be examined for other metals, since these are dissolved away at once from the bulk of the Sn or Sb; but care must be taken that As is not passed over in the presence of Sn.

### PRELIMINARY EXAMINATION.

Note the color, and also if any smell is given off when the substance is rubbed with the hand; also whether it is crystalline or not, and if it is attracted by a magnet (Fe, Ni, Co, etc.). Note also the hardness of the metal; by seeing if it can be scratched or cut by a steel knife; also whether on being struck smartly with a hammer it breaks to powder (brittle), or flattens out (malleable); then try the following experiments:

Experiment.	Observation.	Inference.
468. I.—Heat a small portion on charcoal in the inner blowpipe flame.	The results obtained by (403, and (404) in the preliminary table may be here noticed.	The inference will be found stated in (403) and (404).
469. II.—Heat a portion in a small tube closed at one end.	A metallic sublimate forms.	Presence of Hg, Cd, As; the two latter are detected by (468).
Note.—As and S can frequently only be detected as arsenate and sulphate by fusion with $\text{KNO}_3$ and $\text{Na}_2\text{CO}_3$ , dissolving in water, and testing the solution by (449) or (446).	The sublimate consists of small liquid globules. A yellow sublimate melting to reddish-yellow drops; the substance when heated <i>slowly</i> in a tube open at both ends evolves $\text{SO}_2$ (417).	Presence of Hg.  Presence of S from a sulphide.

# PROCESSES FOR SOLUTION AND EXAMINATION OF A METAL OR ALLOY.

**470. METHOD I.**—Pour some rather dilute HCl upon the powdered metal in a small flask covered with a watch-glass with its concave surface upwards, and heat for some time just short of boiling; if the metal dissolves readily, continue heating until the metal is completely dissolved, and examine the HCl solution according to the general table (419).

Frequently HCl alone does not effect complete solution; two or three drops of strong  $\text{HNO}_3$  should then be poured in, and more  $\text{HNO}_3$  and HCl added occasionally when the action ceases or when red fumes are no longer given off on heating. When the metal has entirely disappeared, add a little more strong HCl and boil as long as any Cl or reddish fumes are given off; then dilute with a little water, heat to boiling, and cool; filter if there is any white residue:

*Residue*, if crystalline, is probably  $\text{PbCl}_2$ , and will be found to dissolve entirely if washed with sufficient boiling water.

In this solution the presence of Pb is confirmed by adding  $\text{K}_2\text{CrO}_4$ , which gives a yellow precipitate soluble in excess of  $\text{KHO}$ , showing *presence of Pb*.

If any residue is left after washing well with boiling water, it is probably  $\text{AgCl}$ ; confirm the presence of Ag by pouring upon the residue hot  $\text{AmHO}$ ; it dissolves completely but is reprecipitated on adding  $\text{HNO}_3$  in excess:

*Presence of Ag.*

*Filtrate* (Note 1): dilute largely with  $\text{H}_2\text{O}$  (see Note 2), and whether this causes a precipitate or not, pass  $\text{H}_2\text{S}$  to saturation into the solution; examine any precipitate thus produced by Table II (435), and proceed to examine the filtrate for Groups III, IV, and V, as directed in the general table (419).

*Note 1.*—If Au and Pt may be present, they must be tested for in the  $\text{H}_2\text{S}$  precipitate, according to the directions in (472-474).

*Note 2.*—A white precipitate appearing on dilution is due to the presence of Bi, Sb, or Sn.

**471. METHOD II.**—Pour upon the finely divided metal some strong  $\text{HNO}_3$ ,<sup>1</sup> and heat in a small flask,

<sup>1</sup> If Hg is found in the preliminary examination and small quantities of Ag have to be tested for, the Hg should be expelled by heating the substance strongly in a porcelain crucible before dissolving in acid, as  $\text{Hg}\cdot\text{NO}_3$  tends to prevent the precipitation of Ag by HCl in Group I.

covered with a watch-glass, as long as any red fumes appear: one of two results will occur:

I.	II.		
<p><i>The substance dissolves completely with or without addition of water.</i> Absence of Pt, Au, Sb, Sn, (Note 1). Examine the solution, after boiling nearly to dryness and diluting with water (Note 2), by the general table (419).</p>	<p><i>A residue is left:</i> add some hot water and boil, then filter and wash the residue on the filter well with boiling water (Note 2). The residue may present the following appearances:</p> <table border="0"> <tr> <td data-bbox="384 425 774 689"> <p>1. <i>Entirely metallic or black powder:</i> probably Pt or Au. Dissolve by heating in a small flask covered with a watch-glass, with a little HCl to which a few drops of <math>\text{HNO}_3</math> have been added. When completely dissolved add more HCl, and boil down in an evaporating-basin nearly to dryness; examine the solution for Au and Pt by (474), commencing with the addition of KCl and using only the left-hand side of the table, since Sn will be absent.</p> </td><td data-bbox="778 425 969 689"> <p>2. <i>White powder</i> may contain Sn, Sb, As, possibly also Pt and Au concealed in it (Note 3).</p> </td></tr> </table>	<p>1. <i>Entirely metallic or black powder:</i> probably Pt or Au. Dissolve by heating in a small flask covered with a watch-glass, with a little HCl to which a few drops of <math>\text{HNO}_3</math> have been added. When completely dissolved add more HCl, and boil down in an evaporating-basin nearly to dryness; examine the solution for Au and Pt by (474), commencing with the addition of KCl and using only the left-hand side of the table, since Sn will be absent.</p>	<p>2. <i>White powder</i> may contain Sn, Sb, As, possibly also Pt and Au concealed in it (Note 3).</p>
<p>1. <i>Entirely metallic or black powder:</i> probably Pt or Au. Dissolve by heating in a small flask covered with a watch-glass, with a little HCl to which a few drops of <math>\text{HNO}_3</math> have been added. When completely dissolved add more HCl, and boil down in an evaporating-basin nearly to dryness; examine the solution for Au and Pt by (474), commencing with the addition of KCl and using only the left-hand side of the table, since Sn will be absent.</p>	<p>2. <i>White powder</i> may contain Sn, Sb, As, possibly also Pt and Au concealed in it (Note 3).</p>		

*Note 1.*—The solution is liable to contain small quantities of these metals, which must always be tested for in a careful analysis.

*Note 2.*— $\text{BiOCl}$  will often precipitate on dilution, but the precipitate will disappear on adding HCl and boiling, being thus easily distinguished from the Group I precipitate.

*Note 3.*—If much residue is obtained a small quantity of it may be heated in a test-tube with HCl adding  $\text{KClO}_3$ ; if it dissolves entirely dissolve the whole of the residue, then examine the solution by Table II, commencing at (435 *b*); if it refuses to dissolve proceed with the rest of the residue as directed below. If the residue is small in quantity examine it at once as directed below.

*Examination of the Non-metallie Residue Insoluble in  $\text{HNO}_3$ .*—Dry the residue on the filter at a gentle heat, mix it thoroughly with about an equal quantity of powdered  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$ , and add the mixture gradually to some  $\text{NaNO}_3$  in fusion in a porcelain crucible; then pour the melted substance out into a porcelain dish; allow it to cool, then pour upon it cold water and let it stand for some time. After crushing the mass with a pestle and stirring it occasionally, filter, and wash the residue on the filter with dilute alcohol, throwing away the washings:

*Residue* may contain Sn, Sb, Pt, Au.

Place it in a small porcelain dish, pour in a little HCl and heat, then add water; whether the residue has dissolved or not place in the liquid a strip of Pt-foil and drop upon it a piece of pure Zn; H is given off; wait until this ceases, taking care that there is some Zn left undissolved, and adding more Zn if the first piece has entirely dissolved. Now remove the platinum strip; if it is stained black *Sb* is present.

The residue in the dish may consist of Sn, Au, and Pt; remove the Zn, rinsing off any substance adhering to it into the dish, stir the liquid in the dish well, then pour off the liquid carefully, leaving the residue; pour in water, stir well, and again pour off carefully. Boil the residue for some time with strong HCl in a test-tube, dilute, decant, add  $\text{HgCl}_2$ ; a white precipitate forms: *Presence of Sn*.

*Residue*: dissolve by warming with HCl and  $\text{HNO}_3$  and examine the solution for Au and Pt by (474), using only the left-hand portion of the table.

*Filtrate* may contain  $(\text{AsO}_4)'''$ : add  $\text{HNO}_3$  until the solution is acid and boil, evaporating the liquid in a dish if very bulky. Pour into half this solution  $\text{AgNO}_3$  as long as it gives any precipitate, and add gradually  $\text{AmHO}$  diluted with 10 or 12 times its bulk of water; a brown precipitate shows:

*Presence of As.*

To the other half of the acid solution add  $\text{AmHO}$  in excess, then  $\text{MgSO}_4$ , and rub the inside of the vessel with a glass rod; a white crystalline precipitate, often appearing only after some time, shows:

*Presence of As.*

## SEPARATION AND DETECTION OF Au AND Pt.

472. Au and Pt will, in the ordinary course of analysis, be entirely precipitated as sulphides in the second group, if  $\text{H}_2\text{S}$  is passed for some time into the hot HCl solution; and since these sulphides are soluble in KHO and in  $\text{Am}_2\text{S}$ , on examining the  $\text{H}_2\text{S}$  precipitate by Table II (435), the Au and Pt will pass into the filtrate when the precipitate is boiled with KHO or  $\text{Am}_2\text{S}$ . No modification of the process described in Table II is required for the detection of these two metals until the examination of the residue in the hydrogen flask is commenced. The Au and Pt will be present in this residue, associated



with Sn if it be present, and usually also with at least a part of the Sb (if present), since Zn and Pt in contact in an acid liquid cause the separation of metallic Sb (193). Accordingly, when Au and Pt have to be tested for, the ordinary course of analysis is to be followed until the residue in the hydrogen flask is obtained; and this is examined as directed in (473).

**473.** After washing the residue left in the hydrogen flask by decantation in a porcelain dish, and removing any excess of Zn, boil it with a little strong HCl in a test-tube for several minutes, allow the residue to settle, and decant the liquid:

**474. Residue:**<sup>1</sup> pour upon the residue in the dish a little HCl, add several drops of HNO<sub>3</sub>, and boil gently very nearly to dryness; add some KCl solution and evaporate once more very nearly to dryness. Pour some absolute alcohol into the cool dish and stir well for a time, allow the precipitate to settle and decant the liquid, wash the precipitate by stirring it with a little more alcohol and decant the liquid when the precipitate has settled:

*Precipitate* will consist of yellow K<sub>2</sub>PtCl<sub>6</sub> and excess of KCl; dissolve it in a little boiling water, pour it into a white dish, add several drops of HCl, then SnCl<sub>2</sub>; an orange-red coloration confirms the

*Presence of Pt.*

*Solution* will be yellow if Au is present; evaporate carefully on a water-bath just to dryness, dissolve in a little water and add a few drops of freshly prepared FeSO<sub>4</sub> solution. Au will be precipitated in a fine powder, causing the liquid to appear reddish by reflected and blue by transmitted light:

*Presence of Au.*

*Solution:* to one part add HgCl<sub>2</sub>; a white precipitate, which does not appear at once if only traces of Sn are present:

*Presence of Sn.*

Pour the other part of this solution into a porcelain dish, immerse it in a strip of Pt and drop a piece of Zn on the Pt: a black stain on the Pt shows:

*Presence of Sb.*

<sup>1</sup> If Sb has not been detected already in the precipitate produced by the gases in AgNO<sub>3</sub> solution (435 *b*) this residue should be examined for Sb, as the Sb, instead of having been given off as SbH<sub>3</sub>, may have been deposited on the Pt or Au. Boil it once more for some time with strong HCl to remove all Sn, wash the residue well by decantation and boil it in the dish with H<sub>2</sub>T adding a few drops of HNO<sub>3</sub>, decant, and test the liquid for Sb by adding HCl and passing H<sub>2</sub>S: the residue is then examined as above (474).

# EXAMINATION OF SUBSTANCES INSOLUBLE IN WATER AND ACIDS.

475. An insoluble substance may consist of one or more of the following substances, all of which are white except  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{FeCr}_2\text{O}_4$ ,  $\text{PbCrO}_4$ , S, C, and  $\text{AgCl}$  which has been exposed to light.

In the following list those substances which are embraced in brackets ( ) may possibly be present, those in square brackets [ ] *improbably*, because they are soluble in water.

1. $\text{BaSO}_4$	Insoluble in water and acids.
2. $\text{SrSO}_4$	“ “ “
3. $[\text{CuSO}_4]$	{ Not perfectly insoluble in water, soluble in hot HCl; hence it should pass into the acid solution.
4. $(\text{PbSO}_4)$	
5. $\text{PbCrO}_4$	Insoluble after being strongly heated.
6. $[\text{PbCl}_2]$	{ Soluble in boiling water, and should therefore have been removed if the residue was well washed with boiling water.
7. $\text{AgCl}$	{ This may have been originally present as such, or may have been derived from the use of HCl in making the solution, or by the action of aqua regia on the insoluble substances $\text{AgBr}$ , $\text{AgI}$ , $\text{AgCy}$ , $\text{Ag}_6\text{Fe}_2\text{Cy}_{12}$ , $\text{Ag}_4\text{FeCy}_6$ . Either uncombined, or as a silicate.
8. $\text{SiO}_2$	{ Insoluble after being strongly ignited, but these are usually dissolved by long boiling with strong HCl.
9. $(\text{Al}_2\text{O}_3)$	
10. $(\text{Fe}_2\text{O}_3)$	
11. $(\text{Cr}_2\text{O}_3)$	
12. $\text{FeCr}_2\text{O}_4$	Chrome iron ore, native.
13. $(\text{SnO}_2)$	Native or ignited.
14. $\text{Sb}_2\text{O}_5, \text{Sb}_2\text{O}_4$	{ Also a few other fluorides, and some metaphosphates and arsenates.
15. $\text{CrF}_2$	
16. S	{ Yellow, slowly soluble in strong $\text{HNO}_3$ , giving red fumes, and yielding $\text{H}_2\text{SO}_4$ .
17. C	{ Black, and quite insoluble.

If sufficient of the substance is at disposal, the preliminary examination (476) may be made on a portion of it. In case the quantity of substance is small, however, the whole of the substance must be employed for the examination by fusion (477).

## 476. PRELIMINARY EXAMINATION.

The substance must be in the state of dry powder. Make a careful examination of it with a pocket lens. Experiments I and II need only be made if the substance is light in color.

Experiment.	Observation.	Inference.
I. Observe whether the substance darkens when allowed to stand in the light for some time.	The color changes to violet or black.	Presence of AgCl.
II. Pour a little $\text{Am}_2\text{S}$ upon a portion of the substance on a watch-glass.	The substance blackens; pass on to III. The substance does not blacken; pass on to V, omitting III and IV, since Pb and Ag must be absent.	Presence of Pb or Ag.
III. Heat some of the substance with a little water and a small piece of KCy; filter off, keeping the residue; to the filtrate add $\text{Am}_2\text{S}$ .	A brownish precipitate.	Presence of AgCl. <i>Confy.</i> On warming some of the substance with $\text{AmHO}$ , filtering, and adding excess of $\text{HNO}_3$ to the filtrate, a white precipitate forms, which, when shaken well or heated, coagulates into flocks.
IV. Wash the residue from Exp. III well upon the filter: a. It is white; drop $\text{Am}_2\text{S}$ upon it. b. It is dark-colored; pour in a little $\text{HA}$ , and boil after adding $\text{AmHO}$ in excess; filter, to the filtrate add $\text{HA}$ in excess and $\text{K}_2\text{CrO}_4$ .	The residue blackens.  A yellow precipitate, soluble in $\text{KHO}$ .	Presence of $\text{PbSO}_4$ or $\text{PbCl}_2$ .  Presence of $\text{PbSO}_4$ or $\text{PbCl}_2$ .
V. Take up some of the substance upon a moistened loop of platinum wire; heat it for a short time in the inner blow-pipe flame, then moisten with a drop of strong $\text{HCl}$ , and hold in the outer part of a Bunsen flame.	A reddish-yellow coloration, dusky-green when seen through the indigo-prism. A crimson-red coloration appearing deep red through the indigo-prism. A yellowish-green coloration. <i>Note.</i> —If all these are present, the colorations may often be seen in succession.	Presence of Ca Presence of Sr Presence of Ba as sulphate.
VI. Heat in a small test-tube or ignition-tube, then strongly on a piece of porcelain or broken glass, or on platinum foil.	A yellow sublimate forms on the sides of tube. When strongly heated the substance smoulders and ultimately burns away.	Presence of S. Presence of C.

Experiment.	Observation.	Inference.
VII. Heat with strong $\text{H}_2\text{SO}_4$ in a platinum crucible or leaden cup covered with a watch-glass (296); or if a silicate is present, examine by passing the gas into $\text{AmHO}$ (297).	The glass is etched. A gelatinous precipitate is obtained in the $\text{AmHO}$ .	Presence of F. Presence of F.
VIII. Fuse some of the substance in a bead of $\text{NaAmHPO}_4$ first in the outer then in the inner blowpipe flame.	Particles are seen floating undissolved in the melted bead. <i>Green-colored bead.</i> <i>Reddish-brown bead, colorless when cold, and becoming greenish in the inner flame.</i>	Presence of $\text{SiO}_2$ (480). Presence of Cr. Presence of Fe.

## EXAMINATION OF INSOLUBLE SUBSTANCES.

477. Mix the finely powdered substance<sup>1</sup> with three or four times its weight of fusion mixture, and heat the mixture in a small covered porcelain crucible<sup>2</sup> until it melts; keep it in fusion for at least ten minutes. Allow the crucible to cool, then pour some water into it and allow to stand or boil until the solid mass is loosened from the crucible; boil this in a porcelain dish with distilled water, crushing the mass by pressure with a pestle if it does not quickly fall to pieces. Allow the residue to settle, pour off the solution through a filter, and boil the residue with a little more water; pour off through the same filter, adding this filtrate to the former one.

For the examination of the undissolved residue see (478), for the filtrate (479).

478. *Residue on the filter*; wash well with boiling water, then make a hole in the bottom of the filter, wash

<sup>1</sup> Which, if it is found by Exp. VI to contain free S or C, must first be heated strongly for some time in an open porcelain crucible.

<sup>2</sup> If Pb and Ag have been proved to be absent by the preliminary tests, or if they have been first removed by boiling the substance with  $\text{KCy}$  solution, then with  $\text{HAc}$  and excess of  $\text{AmHO}$  and washing well, a platinum crucible may be used. The use of a platinum crucible is preferable, since after fusing in porcelain small quantities of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  will always be found, being derived from the action of the  $\text{Na}_2\text{CO}_3$  on the glaze of the porcelain.

the residue through into a test-tube by pouring upon it a little boiling dilute  $\text{HNO}_3$  (see Note 1 below), and boil; the residue dissolves entirely if the fusion has been continued sufficiently long (see Note 2). Filter if necessary, and examine the solution by the general table (419), bearing in mind that only the metals enumerated in (475) are likely to be present (Note 3).

*Note 1.*—If Ag and Pb are known to be absent by the preliminary experiments, HCl may be used for dissolving the residue and is preferable; if effervescence is produced by these acids the presence of Ba, Sr, Ca, or Mg is proved.

*Note 2.*—A residue here may consist of chrome iron ore; this may be dissolved by heating with  $\text{HNO}_3$  and  $\text{KClO}_3$ , and the solution tested by the general table, when Cr and Fe will be found.

*Note 3.*—It is best to evaporate the solution quite to dryness before testing for Group III, using a water-bath towards the end if the substance spirts. This is always necessary if  $\text{SiO}_2$  is present in the substance, since it is sometimes obtained in the acid solution, and is by this means at once separated.

**479. Aqueous Solution of the Fused Mass.**—Divide into two parts, A and B.

A. Add HCl until the liquid is distinctly acid, and evaporate in a porcelain dish to dryness, finishing the process on a water-bath if necessary to avoid spirting; then continue to heat the dish gently until the residue is quite dry; pour in a little strong HCl and warm, dilute and heat again; an insoluble residue shows *presence of*  $\text{SiO}_2$ .

Filter, and examine the filtrate by the general table (419) more particularly for Al, but other bases should also be tested for, which being soluble in alkalies may pass into this solution, such as Cr, Mn, Zn, Sn.

B. Test separate portions for the following acid-radicals as described below:

1. *Chloride*: acidify with  $\text{HNO}_3$  and add  $\text{AgNO}_3$ ; white precipitate easily soluble in  $\text{AmHO}$ .
2. *Sulphate*: acidify with HCl and add  $\text{BaCl}_2$ ; white precipitate insoluble on boiling.

*Note.*—Unless the fusion mixture employed was free from chloride and sulphate, Tests 1 or 2 are worthless.



3. *Chromate*: acidify with  $\text{H}\bar{\text{A}}$  and add  $\text{Pb}\bar{\text{A}}_2$ ; yellow precipitate; a chromate is seen also by the yellow color of the solution. Cr thus detected may have been present acting as a metal or as a constituent of an acid-radicle.
4. *Phosphate*: acidify with  $\text{HNO}_3$ , add a few drops to  $\text{AmHMoO}_4$  solution and warm gently. A yellow precipitate forms, often only after a time, or on gently heating. If As has been found on passing  $\text{H}_2\text{S}$  into the hot  $\text{HCl}$  solution,  $(\text{PO}_4)'''$  must be tested for in a portion of the filtrate after boiling off  $\text{H}_2\text{S}$ , else the above yellow precipitate may be due to  $(\text{AsO}_4)'''$ .
5. *Fluoride*: add  $\text{HCl}$  in excess to a part of the solution, stir well, and let stand until the  $\text{CO}_2$  has escaped, then add  $\text{AmHO}$  in excess, then  $\text{CaCl}_2$  as long as it produces any precipitate, and let stand for a time; filter off, dry the precipitate and examine it for F by pouring strong  $\text{H}_2\text{SO}_4$  upon it in a platinum crucible covered with a watch-glass (296).

## ANALYSIS OF SILICATES.

480. The presence of silica is shown by Exp. VIII in the preliminary examination of insoluble substances (476); when it has been found it becomes necessary to examine for all metals, since many silicates which are soluble when alone, become insoluble when mixed or combined with insoluble silicates.

The ordinary analytical course requires but slight modification to adapt it to the examination of silicates. Many silicates are entirely decomposed by heating with strong  $\text{HCl}$  for some time just short of boiling; if this decomposition has been effected, only a colorless residue of silicic acid will remain, which may be identified by its solubility in hot  $\text{Na}_2\text{CO}_3$  solution.

If the silicate is not completely decomposed by hot strong  $\text{HCl}$ , some of it must be fused with fusion mixture as directed in (477), and the cool residue boiled with water; the solution and residue are then examined by (478) and (479), remembering, however, that all metals may be present.

481. Since Na and K cannot be tested for in the solution obtained after fusion, a separate portion must be examined for K and Na by one of the following processes:

I. Evaporate the powdered substance several times in a platinum dish or crucible either with hydrofluoric acid and subsequently with strong  $\text{H}_2\text{SO}_4$ , or with five times its weight of calcium fluoride mixed into a paste with strong  $\text{H}_2\text{SO}_4$ , in either case heating finally until no more white fumes are evolved. Boil the cool residue with water, add  $\text{BaCl}_2$  solution as long as it causes any precipitate, then add  $\text{AmHIO}$  in excess and  $\text{Am}_2\text{CO}_3$  as long as it causes any precipitate, filter and examine the filtrate for K and Na by Table V (439).

II. Mix the powdered substance intimately with four times its weight of barium hydrate, and heat strongly in a platinum crucible for about half an hour; dissolve the cool mass in dilute  $\text{HCl}$ , add  $\text{AmHIO}$  in excess and then  $\text{Am}_2\text{CO}_3$  in excess, filter, rejecting the precipitate; evaporate the filtrate to dryness, ignite the residue, then boil it with water; add a little  $\text{HCl}$  to the solution and test for K and Na by Table V (439).

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## 482. ANALYSIS OF SUBSTANCES CONTAINING CYANOGEN.

If a small quantity of the substance to be analyzed, when examined by (304) or (306), is found to contain cyanogen, the usual course of analysis must be somewhat modified, since the presence of cyanogen would produce confusing results. The cyanogen may be present as a

cyanide, sulphocyanide, ferrocyanide, ferricyanide, or cobalticyanide, rarely as a manganocyanide or chromicyanide. Since the method to be adopted when a cyanide or sulphocyanide only is present is much more simple than that rendered necessary by the presence of the other cyanogen compounds above mentioned, it is advisable first to ascertain in what form the cyanogen occurs, by the following preliminary experiments made on a small portion of the substance; according to the results yielded by these experiments the further examination of the substance is made by Method I (484) or by Method II (485).

### PRELIMINARY EXAMINATION.

**483.** Boil a portion of the substance for several minutes with KHO solution, then add some  $\text{Na}_2\text{CO}_3$  solution as long as it causes any precipitate, and boil again for several minutes; filter, make the cold filtrate just acid with HCl, filter if necessary, and test separate portions as follows:

Reagent added.	Result.	Inference.
1. $\text{FeSO}_4$ solution, . . . .	{ Blue precipitate, . . White precipitate, . .	Presence of $(\text{FeCy}_6)^{\text{iv}}$ $(\text{FeCy}_6)_2^{\text{vi}}$ Probable presence of $(\text{CoCy}_6)_2^{\text{vi}}$
2. $\text{Fe}_2\text{Cl}_6$ solution, . . . .	{ Blue precipitate, . . Blood-red coloration	Presence of $(\text{FeCy}_6)^{\text{iv}}$ Presence of $(\text{CyS})$ .
3. $\text{ZnSO}_4$ solution as long as it causes any precipitate, . . . .	{ Light-brown precipitate, . . . . White precipitate, . .	{ Presence of $(\text{FeCy}_6)_2^{\text{vi}}$ Presence of $(\text{FeCy}_6)^{\text{iv}}$ , $(\text{CoCy}_6)_2^{\text{vi}}$ .
<i>Confirmatory.</i> —Filter off the precipitate, add $\text{ZnSO}_4$ solution to the filtrate, and if it causes any precipitate, pour again through the filter, repeating this process until no further precipitate is produced by $\text{ZnSO}_4$ . Fuse some of the precipitate in a clear borax bead, . . . . .		{ A blue bead is produced, . . . . } Presence of $(\text{CoCy}_6)^{\text{vi}}$

If these preliminary tests show the presence of  $(\text{FeCy}_6)^{\text{iv}}$ , substance by Method II (485). If the absence of these acid-radicals which indicate their presence, proceed according to Method I.

If none of the above acid-radicles are found in the preliminary analytical course is to expel  $\text{HCy}$  by boiling after adding  $\text{HCl}$ .

**484. METHOD I.**—If  $(\text{CyS})'$  is present, boil the portion of  $\text{HNO}_3$  for some time, dilute a little and boil again. If any residue the residue as directed at the end of (420), any undissolved  $\text{HNO}_3$  solution is evaporated nearly to dryness and examined.

Another portion of the substance is examined for acid-radicles.

**485. METHOD II. (Fresenius).**—Boil the substance with washings to the filtrate:

<p><i>Filtrate:</i> examine this for metals, more especially the alkalies, and for acid-radicles according to the directions given for analyzing a liquid (380).</p>	<p><i>Residue:</i> boil with <math>\text{KHO}</math> solution for several minutes, then add and boil again; filter and wash the residue:</p>		
<p>The acid-radicles should be first tested for in a portion of the solution and if <math>(\text{FeCy}_6)^{\text{iv}}</math>, <math>(\text{Fe}_2\text{Cy}_{12})^{\text{vi}}</math>, <math>(\text{Co}_2\text{Cy}_{12})^{\text{vi}}</math>, one or more be found, the solution must be evaporated to dryness with <math>\text{HNO}_3</math>, and the residue strongly heated (see general table) after filtering from the <math>\text{H}_2\text{S}</math> precipitate, in order to destroy these cyanogen radicles. The Fe, Co, etc., in the cyanogen acid-radicles will then be detected in the general table.</p>	<p><i>Filtrate:</i> pass <math>\text{H}_2\text{S}</math>, and if it causes any precipitate continue <math>\text{KHO}</math>,<sup>1</sup> heat and filter:</p>		
	<p><i>Precipitate:</i> wash well with boiling water, and boil the precipitate with strong <math>\text{HNO}_3</math>, a black residue of <math>\text{HgS}</math> may remain; filter this off after diluting the acid, and confirm the presence of <math>\text{Hg}</math> in the precipitate by heating it with <math>\text{Na}_2\text{CO}_3</math> in a bulb-tube (147).</p> <p>The filtrate (or solution if <math>\text{HgS}</math> is absent) is evaporated to dryness, the residue is then dissolved in a little hot strong <math>\text{HCl}</math>, the solution is much diluted, saturated with <math>\text{H}_2\text{S}</math>, and filtered:</p>		
	<table border="0"> <tr> <td data-bbox="367 1067 585 1137"><i>Precipitate:</i> examine for Pb and Cu by Table II (435 a).</td> <td data-bbox="595 1067 1010 1314"> <p><i>Filtrate:</i> add <math>\text{AmCl}</math>, <math>\text{AmHO}</math> in excess, and <math>\text{Am}_2\text{S}</math>, and examine for Zn, Mn, Ni, Co, etc., by Table III c<sub>2</sub> (465).</p> </td> </tr> </table>	<i>Precipitate:</i> examine for Pb and Cu by Table II (435 a).	<p><i>Filtrate:</i> add <math>\text{AmCl}</math>, <math>\text{AmHO}</math> in excess, and <math>\text{Am}_2\text{S}</math>, and examine for Zn, Mn, Ni, Co, etc., by Table III c<sub>2</sub> (465).</p>
<i>Precipitate:</i> examine for Pb and Cu by Table II (435 a).	<p><i>Filtrate:</i> add <math>\text{AmCl}</math>, <math>\text{AmHO}</math> in excess, and <math>\text{Am}_2\text{S}</math>, and examine for Zn, Mn, Ni, Co, etc., by Table III c<sub>2</sub> (465).</p>		
	<p><i>Filtrate:</i> add dilute saturation and filter:</p>		
	<p><i>Precipitate:</i> boil with <math>\text{KHO}</math>, filter off any black precipitate and examine it for Hg by heating it with <math>\text{Na}_2\text{CO}_3</math> in a bulb-tube (147).</p>		
	<p>Add to the filtrate or solution <math>\text{HCl}</math> until it is acid, pass <math>\text{H}_2\text{S}</math> to saturation, and examine for As, Sb, Sn, Pt, Au, by Table II (435), commencing at (435 b).</p>		

<sup>1</sup> If  $\text{H}_2\text{S}$  causes a precipitate to form,  $\text{NaHS}$  or  $\text{KHS}$  may be added, drop by drop; this may be done instead of passing  $\text{H}_2\text{S}$  to saturation and then adding  $\text{KHO}$ .

( $\text{FeCy}_6$ )<sup>vi</sup>, ( $\text{CoCy}_6$ )<sup>vi</sup>, one or more, examine the remainder of the cles is indicated by not obtaining the results in the second column (484).

nary experiments, the only modification requisite in the ordinary in preparing the solution (383) or in testing for Group I (419). the substance which is to be examined for metals with strong due remains decant the solution and proceed to endeavor to dis-residue being then examined according to (475 *et seq.*). The by (419).

in the usual way.

water, filter, and wash the residue with boiling water, adding the

some  $\text{Na}_2\text{CO}_3$  solution as long as it causes any precipitate in the solution or the filtrate,

to pass the gas until the liquid is saturated, then add more

$\text{HNO}_3$ , gradually until the liquid is just acid, pass  $\text{H}_2\text{S}$  to

*Filtrate*: Divide into two parts,  $\alpha$ ,  $\beta$ :

$\alpha$ . Examine for acid-radic-  
cles in the usual way,  
testing for ( $\text{Co}_2\text{Cy}_{12}$ )<sup>vi</sup>  
by adding excess of  
 $\text{ZnSO}_4$ , filtering and try-  
ing whether the precipi-  
tate gives a blue bead  
with borax.

$\beta$ . Evaporate to dryness and fuse  
the residue: when cold, boil it  
with water and filter:

*Residue*: dis-  
solve in  $\text{HCl}$ ,  
and test for  $\text{Al}$ ,  
 $\text{Fe}$ ,  $\text{Mn}$ ,  $\text{Co}$   
(465); the last  
three if found  
were present  
as cyanogen  
acid-radicles.

*Filtrate*: acidify  
a portion if  
yellow with  
 $\text{H}^+\text{A}$  and add  
 $\text{PbA}_2$ ; a yel-  
low precipitate  
shows ( $\text{CrO}_4$ )<sup>vi</sup>,  
the  $\text{Cr}$  having  
been present  
as cyanogen  
acid-radicle.

Test another  
part for  $\text{Al}$  by  
adding  $\text{HCl}$  in  
excess, then  
 $\text{AmHO}$  in ex-  
cess.

*Residue*: dissolve and  
examine for metals  
in the usual manner  
(383).

$\text{Fe}$ ,  $\text{Co}$ ,  $\text{Mn}$ ,  $\text{Cr}$ , if  
found in this residue,  
were not present as  
( $\text{FeCy}_6$ )<sup>iv</sup>, ( $\text{Fe}_2\text{Cy}_{12}$ )<sup>vi</sup>,  
( $\text{Co}_2\text{Cy}_{12}$ )<sup>vi</sup>, etc.

drop, until it no longer gives any precipitate in the liquid or in the filtrate;



486. The advantage of employing this somewhat complicated and tedious method of Fresenius is that it usually enables the analyst to ascertain whether Fe, Co, Mn, Cr, when present, form a part of a complex cyanogen acid-radicle or simply act as metals combined with acid-radicles. For if Fe, Co, Mn, Cr, are found in the residue left after boiling with  $\text{KHO}$  and  $\text{Na}_2\text{CO}_3$ , they were present in the latter form; if found in the alkaline filtrate they were present as cyanogen acid-radicles; if they were detected as cyanogen acid-radicles in the aqueous solution they were entirely present in that solution in that form, although they will also be detected in the examination for metallic-radicles; if they were detected only as metallic-radicles and not as cyanogen acid-radicles, they were present as metallic-radicles in the aqueous solution.

487. The following two processes have been proposed for removing cyanogen from a substance before analysis, after which the substance may be examined for metals in the usual way (382 *et seq.*); but these methods, though much more easy and rapid, are less perfect than the preceding ones, since Fe, Co, Mn, Cr, if detected, may have been present either as cyanogen acid-radicles, or as metals united with an acid-radicle, or in both forms.

1. Pour upon the powdered substance strong  $\text{H}_2\text{SO}_4$  in a porcelain crucible, evaporate to dryness, and ignite the residue strongly; when cold dissolve it by heating with a little strong  $\text{HCl}$ , adding water and heating again. (Rose.)

2. "Cyanogen compounds are best destroyed by fusion in a porcelain crucible with 3 or 4 times their weight of a mixture of 3 parts of  $\text{Am}_2\text{SO}_4$  and 1 part of  $\text{AmNO}_3$ ." The residue left in the crucible is dissolved and examined for metals in the usual way.

## EXAMPLE SHOWING HOW TO ENTER THE RESULTS OF ANALYSIS OF A COMPLEX SUBSTANCE.

The substance given for analysis consisted of a powder containing pink, blue, white, and black particles. It smelt faintly of ammonia.

### 488. PRELIMINARY EXAMINATION FOR METALS.

Experiment.	Observation.	Inference.
EXPT. I.—Heated in a small dry test-tube.	Water given off which turned red litmus-paper blue. Strong smell of $\text{NH}_3$ -gas. Substance blackened, no smell of burning.	Pres. of $\text{H}_2\text{O}$ . Pres. of $\text{NH}_4$ . Pres. of $\text{NH}_4$ . Prob. pres. of Co, Cu, and abs. of T and A.
Confy.—Held in the upper part of the tube a glass rod with a drop of lime-water hanging on its end.	Slight white sublimate. The lime-water became milky. Brown nitrous fumes evolved, recognized by their smell. Cl-gas evolved, found by smell and bleaching litmus.	Pres. of As, $\text{NH}_4$ , Hg. $\text{CO}_2$ evolved. Pres. of nitrate.
Confy.—Boiled a portion of the substance with KHO solution.	$\text{NH}_3$ -gas was evolved, recognized by its smell, and by giving white fumes with strong HCl.	Pres. of Cl.
Confy.—Heated strongly another portion of the dried substance with $\text{Na}_2\text{CO}_3$ in a bulb-tube.	No mirror formed.	Pres. of $\text{NH}_4$ . Abs. of Hg and As.
EXPT. II.—Heated a portion of the substance on a loop of platinum wire in the Bunsen flame, moistened with HCl and heated again in the flame.	Bright-yellow flame. The flame appeared crimson through the indigo-prism.	Pres. of Na. Pres. of K.
Heated for some time in the tip of the inner blowpipe flame, moistened with HCl, and again held in the Bunsen flame.	Crimson col <sup>r</sup> appearing intense red through the indigo-prism. Bright-green col <sup>r</sup> with blue core.	Pres. of Sr. Pres. of Cu.

Experiment.	Observation.	Inference.
EXPT. III.—Heated a portion of the substance on charcoal in the inner blowpipe flame.	The greater part of the substance fused readily, and was absorbed by the charcoal. Deflagration occurred. A red metallic residue remained.	Pres. of a salt of K, Na. Pres. of chlorate, nitrate. Pres. of Cu.
<i>Confy.</i> —Fused in a clear borax bead in the outer and inner blowpipe flames.	In the outer flame a bead <i>green</i> whilst hot, <i>blue</i> when cold. In the inner flame <i>red</i> and <i>nearly opaque</i> .	Pres. of Cu.
<i>Confy.</i> —Fused on platinum foil with $\text{Na}_2\text{CO}_3$ $\text{KNO}_3$ .	No <i>bluish-green</i> or <i>yellow</i> mass on cooling.	Abs. of Mn and Cr.
<i>Confy.</i> —Fused on charcoal in the inner blowpipe flame with $\text{Na}_2\text{CO}_3$ .	Red metallic residue. A portion placed on a silver coin and moistened gave no black stain.	Pres. of Cu. Abs. of S.

### 489. PRELIMINARY EXAMINATION FOR ACID-RADICLES.

Experiment.	Observation.	Inference.
EXPT. I.—Added dilute HCl without heating.	A colorless gas was evolved, which was free from smell, and turned a drop of lime-water milky.	Pres. of carbonate. Abs. of sulphite, hypochlorite, etc.
Heated to boiling.	Cl was evolved, recognized by its smell and by bleaching moist litmus-paper.	Pres. of nitrate, chlorate, or some other oxidizing substance.
EXPT. II.—Added strong $\text{H}_2\text{SO}_4$ .	A bright-yellow chlorous gas evolved, which cracked when warmed.	Pres. of chlorate.
<i>Confy.</i> —Dropped in copper turnings and heated.	Reddish-brown fumes evolved.	Pres. of nitrate.
Heated strongly, cooled, and rinsed out.	The tube when dry was seen not to be etched.	Abs. of fluoride.
<i>Confy.</i> —Boiled a portion of the substance with water, added strong $\text{H}_2\text{SO}_4$ , cooled and poured in $\text{FeSO}_4$ solution carefully.	A brown ring formed on the surface of the acid.	Pres. of nitrate.

**490. EXAMINATION FOR METALS IN THE WET WAY.**

Boiled a portion of the substance with  $\text{Fe}_2\text{Cl}_6$ ,  $\text{FeSO}_4$  and  $\text{KHO}$ , added  $\text{HCl}$  in excess, no blue pp.: *Absence of Cy.*

Proceeded to dissolve the substance and examine the solution by the general table.

(*Continued on page 296.*)

Boiled a portion of the substance with water; as it did not HCl poured upon the undissolved residue; effervescence occurred, as long as any smell of Cl was perceived; the substance was water sol<sup>n</sup>. which had been proved previously to give no pp.

<i>No pp.</i> <i>Abs. of Group I.</i> <i>Hg', Ag, and prob. Pb.</i>	Diluted with water and passed H <sub>2</sub> S until the liquid smelt strongly <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <i>A black pp.</i>  <i>Exam<sup>d</sup> by Table II.</i> </div> <div style="width: 45%;"> <i>Filtrate</i> which gave no further pp. with Boiled until it no longer smelt of H<sub>2</sub>S, on addition of HNO<sub>3</sub> (<i>prob. pres. of Fe</i>), of the HCl sol<sup>n</sup> to some AmHMoO<sub>4</sub> boiled; filtered:   <i>A brown pp.</i>  <i>Exam<sup>d</sup> by Table III A.</i> </div> </div>	
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#### 491. EXAMN. OF PP. IN GROUP II.

Removed from the filter into a porcelain dish and boiled with KHO filtered:

<i>Filtrate:</i> Acidified with HCl, a white milky liquid only: <i>Abs. of Group II B.</i>	<i>Pp. removed from filter by a glass rod into a porcelain dish and boiled with strong HNO<sub>3</sub> as long as any red fumes came off, added dilute H<sub>2</sub>SO<sub>4</sub> and stirred well:</i>		
	<i>No. pp.:</i> <i>Abs. of Hg and Pb.</i>	Added to sol <sup>n</sup> excess of AmHO; blue solution ( <i>pres. of Cu</i> ):	
		<i>No pp.</i> <i>Abs. of Bi.</i>	Acidified the blue sol <sup>n</sup> with HCl and saturated with H <sub>2</sub> S; filtered off the black pp. rapidly and boiled it with dilute H <sub>2</sub> SO <sub>4</sub> :  <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <i>Pp.:</i> dissolved in a little boiling dilute HNO<sub>3</sub>, added AmHO in excess, then excess of H<sub>2</sub>A, then K<sub>2</sub>FeCy<sub>6</sub>; chocolate-red pp.:  <i>Pres. of Cu.</i> </div> <div style="width: 45%;"> <i>Filtrate:</i> diluted much and passed H<sub>2</sub>S; no pp.:  <i>Abs. of Cd.</i> </div> </div>

#### EXAMN. OF PP. IN GROUP III A.

Dissolved in a little boiling dilute HCl, added pure NaHO in excess, boiled and filtered:

<i>Filtrate:</i> added HCl gradually till the liquid became acid (no pp.), then AmHO in excess; no pp.: <i>Abs. of Al.</i>	<i>Pp.:</i> dried and fused on platinum foil with Na <sub>2</sub> CO <sub>3</sub> and KNO <sub>3</sub> , boiled the colorless <i>abs. of Cr</i> mass when cold with water; decanted from the undissolved residue:  <i>Residue</i> in the dish dissolved by boiling with a little HCl, added several drops of KCyS; a blood-red coloration: <i>Pres. of Fe.</i>	
		<i>Soln.</i> being colorless proved <i>abs. of Cr.</i> Acidified with H <sub>2</sub> A, boiled, and added PbA <sub>2</sub> ; no yellow pp.: <i>Abs. of Cr.</i>



completely dissolve, the sol<sup>n</sup>. was decanted, and a little dilute and on boiling, Cl was smelt. Added a little strong HCl, boiled completely dissolved. Cooled this sol<sup>n</sup>. and mixed it with the on addition of a little dilute HNO<sub>3</sub>:

of the gas, filtered :

H<sub>2</sub>S was pink (*prob. pres. of Co*).

Added some strong HNO<sub>3</sub> and boiled to dryness, the color of the sol<sup>n</sup> changed to light-brown warmed the residue with HCl, it dissolved completely *abs. of H<sub>2</sub>SiO<sub>3</sub>*. Added a small portion warmed; no pp.: *Abs. of PO<sub>4</sub>'''*. To the rem<sup>t</sup> added AmCl, then excess of AmHO, and

Filtrate was again pink (*presence of Co*): added much Am<sub>2</sub>S and boiled, filtered :

A black pp.

Exam<sup>d</sup> by Table III B.

Filtrate was yellow (*absence of Ni*): added Am<sub>2</sub>CO<sub>3</sub>, filtered :

A white pp.

Exam<sup>d</sup> by Table IV.

Filtrate.

Exam<sup>d</sup> by Table V.

### EXAM<sup>N</sup>. OF PP. IN GROUP III B.

Rinsed the pp. off the filter with some cold dilute HCl, stirred well, filtered :

Pp. was black and had already been proved to contain no Ni; fused a portion into a clear borax bead, bead blue in both flames:

*Pres. of Co.*

Filtrate: boiled until it no longer smelt of H<sub>2</sub>S, added a crystal of KClO<sub>3</sub>, boiled until the smell of Cl ceased, cooled and added pure NaHO in excess;

No pp.  
*Abs. of Mn.*

Passed H<sub>2</sub>S into the sol<sup>n</sup>;  
no pp.:  
*Abs. of Zn.*

### EXAM<sup>N</sup>. OF PP. IN GROUP IV.

1. *Exam<sup>n</sup>. by Flame col<sup>n</sup>.*—Dissolved a small quantity of the pp. in a few drops of HCl upon a watch-glass, dipped a loop of Pt-wire into the sol<sup>n</sup>. and held it in the Bunsen flame; a crimson-red color was imparted to the flame, which appeared intense red through the indigo-prism: *Pres. of Sr.* This coloration was followed by a yellowish-green very persistent col<sup>n</sup>: *Pres. of Ba.*

2. *Exam<sup>n</sup>. in the Wd Way.*—Dissolved the rest of the pp. in as little boiling H<sub>2</sub>A as possible; to a small part of the sol<sup>n</sup>, perfectly cold, added CaSO<sub>4</sub> sol<sup>n</sup>; an immediate pp. formed: *Pres. of Ba.*

To the remainder of the  $\text{H}\bar{\text{A}}$  sol<sup>n</sup>, proved to be acid to litmus, added  $\text{K}_2\text{CrO}_4$  until the liquid appeared yellow, warmed and poured through a double filter:

*Pp.*, which contained all the Ba present, was rejected.

To the clear *filtrate*, which was orange-red in color, added  $\text{AmHO}$  until the color changed to light yellow, then added  $\text{Am}_2\text{CO}_3$  in excess and filtered;

*Filtrate* was rejected.

*Pp.*: dissolved in as little boiling  $\text{H}\bar{\text{A}}$  as possible; added to a small portion of the sol<sup>n</sup>  $\text{CaSO}_4$  sol<sup>n</sup> and boiled, a pp. formed, showing *pres. of Sr*.

To the remainder of the  $\text{H}\bar{\text{A}}$  solution added  $\text{H}_2\text{SO}_4$ , boiled, filtered, and to the filtrate, which gave no pp. after being boiled with more  $\text{H}_2\text{SO}_4$ , added  $\text{AmHO}$  in excess and  $\text{Am}_2\text{C}_2\text{O}_4$ , no pp.:  
*Abs. of Cu.*

#### EXAMS. OF FILTRATE FROM GENERAL TABLE FOR GROUP V.

Evaporated the filtrate to dryness in a porcelain dish, scraped out the residue upon platinum foil, and ignited strongly until white fumes ceased to appear; dissolved the residue off the foil by boiling with water to which several drops of  $\text{HCl}$  had been added, divided the sol<sup>n</sup> into two unequal parts:

To the larger portion added several drops of  $\text{H}_2\text{SO}_4$  and boiled, then  $\text{AmHO}$  in excess and several drops of  $\text{Am}_2\text{C}_2\text{O}_4$ ; on heating, a slight pp. formed; filtered, and added to the clear filtrate  $\text{Na}_2\text{HPO}_4$ ; a white crystalline pp.:

*Pres. of Mg.*

Into the smaller portion dipped a loop of platinum wire, and held it in the Bunsen flame; an intense yellow col<sup>r</sup>:

*Pres. of Na,*

appearing crimson through the indigo-prism:

*Pres. of K.*

Confirmed the pres. of K by stirring a fresh portion of the sol<sup>n</sup> with  $\text{PtCl}_4$  on a watch-glass; a yellow pp. formed.

Metals found: Cu, Fe, Co, Ba, Sr, Mg, Na, K,  $\text{NH}_4$ .

### 492. EXAM<sup>N</sup>. FOR ACID-RADICLES.

The following acid-radicles have already been detected:  $(\text{CO}_3)''$ ,  $(\text{NO}_3)'$ ,  $(\text{ClO}_3)'$ .

By reference to the table of solubilities (455), under the columns corresponding to the above metals, the only salt insoluble in acids is found to be  $\text{BaSO}_4$ ; since Ba is present, and the substance is entirely soluble in acids,  $(\text{SO}_4)$  is *absent*.

The following acid-radicles have also been proved to be absent in the general examination for metals:

$(\text{CrO}_4)''$ , by the  $\text{HCl}$  solution not becoming green on passing  $\text{H}_2\text{S}$ .

$(\text{AsO}_3)'''$  and  $(\text{AsO}_4)'''$ , by no pp. forming in Group II B.

$(\text{SiO}_3)''$  and  $(\text{SiF}_6)''$ , by no residue insoluble in  $\text{HCl}$  remaining on evaporating to dryness with  $\text{HCl}$  for Group III A.

$(\text{PO}_4)'''$ , by testing with  $\text{AmHMoO}_4$  in the  $\text{HCl}$  sol<sup>n</sup>. for Group III A.

The organic acid-radicles  $\bar{\text{A}}$  and  $\bar{\text{T}}$  are absent, since there was no smell of burning on heating the substance.

The only commonly occurring acid-radicles remaining to be specially tested for are therefore Cl, Br, I,  $(\text{C}_2\text{O}_4)''$ , and  $(\text{BO}_3)'''$ ; and of these Br and I are probably absent, since no violet fumes of I or brown fumes of Br were evolved with strong  $\text{H}_2\text{SO}_4$ .

Boiled a portion of the substance with pure  $\text{Na}_2\text{CO}_3$  sol<sup>n</sup>. and filtered; acidified portions of the filtrate with—

$\text{HNO}_3$	$\text{H}\bar{\text{A}}$
<p><i>Added <math>\text{AgNO}_3</math>; a perfectly white pp., easily sol. in <math>\text{AmHO}</math>:</i></p> <p><i>Pres. of Cl.</i></p>	<p><i>Added <math>\text{CaSO}_4</math>; no pp.:</i></p> <p><i>Abs. of <math>(\text{C}_2\text{O}_4)''</math>.</i></p>
<p>Moistened a piece of turmeric-paper with <math>\text{HCl}</math> sol<sup>n</sup>. of the substance and dried at <math>100^\circ</math>; no brown stain produced.</p> <p><i>Abs. of <math>(\text{BO}_3)'''</math>.</i></p>	

493. Found { *Metallic-radicles:* Cu, Fe, Co, Ba, Sr,  
Mg, Na, K,  $\text{NH}_4$ .  
*Acid-radicles:*  $\text{CO}_3$ ,  $\text{NO}_3$ ,  $\text{ClO}_3$ , Cl.

## SECTION VII.

### APPARATUS, REAGENTS, ETC., REQUIRED FOR THE FOREGOING COURSE.

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#### LIST OF APPARATUS REQUIRED BY EACH STUDENT.

494. The following list is so arranged that :

Division I contains all apparatus which is required only for the experiments given in Section I.

Division II is apparatus required both for Section I and for the Sections on Analysis.

Division III is apparatus used only in analysis.

Hence a student intending only to perform the experiments in Section I will require the apparatus in Divisions I and II. If he is omitting this portion and intends only to work through the Sections on Analysis, he must be furnished with the apparatus in Divisions II and III, and will not require that in Division I.

*Note.*—Apparatus contained in large brackets [ ] is useful but not indispensable; the asterisk marks apparatus which may be kept for general use, and need not then be supplied to *each* student.

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#### DIVISION I. (See note at end of list, page 303.)

- \*1 Wide-mouthed, stoppered, white-glass gas-jar; about 24 oz. capacity, and 2 inches inside across the neck, whose upper edge should be ground so as to be closed with a ground-glass plate.
- \*1 Small-flanged cylinder, 6 inches in height,  $1\frac{1}{4}$  inches internal diameter, ground at the edge.
- \*1 Deflagrating spoon, brass cap  $2\frac{1}{2}$  inches across.
- \*1 Small two-necked Woulfe's bottle, not less than 4 oz. capacity; or a small wide-necked bottle of not less capacity.



- \*1 Small retort, best tubulated with stopper, about 4 to 6 oz. capacity.

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## DIVISION II.

- 6 Test-tubes, 5 or 6 inches long, and from  $\frac{1}{2}$  to  $\frac{3}{4}$  inch in diameter.
- 1 Test-tube cleaner.
- 2 Lengths of hard glass tubing, rather more than  $\frac{1}{8}$ th inch internal diameter.
- \*1 Thistle funnel.
- \*[1 Clock glass, about 4 inches across.]
- 1 Round ground-glass plate, 3 inches across.
- 2 Porcelain dishes, one  $2\frac{1}{2}$  inches across, one 3 inches across.
- 2 Watch-glasses, about 2 inches across.
- 1 Small flask, about 4 oz. capacity.
- \*Red or black india-rubber tubing; one piece 18 inches long and  $\frac{5}{16}$  inch internal diameter,<sup>1</sup> one piece 6 inches long and  $\frac{3}{16}$  inch internal diameter.
- \*1 Bunsen burner<sup>1</sup> with separate rose-top.
- 1 Small pestle and mortar.
- 1 Iron tripod-stand.
- 1 Piece of wire gauze, 5 inches square.
- \*1 Round file.
- \*1 Triangular file.
- \*1 Small set of cork-borers.
- \*1 Small retort-stand, 12 inches in height, and fitted with 3 brass rings.

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## DIVISION III.

- 4 Glass funnels, two 2 inches across at the top, two  $2\frac{1}{2}$  inches across at the top.
- [2 Tobacco-pipe cleaners, for cleaning glass tubes.]
- 2 Boiling tubes, 6 or 7 inches long, from  $1\frac{1}{4}$  to  $1\frac{1}{2}$  inch across.

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<sup>1</sup> The Bunsen burner and gas-tubing may be fixtures on each working bench, and will not then be purchased by each student.

- 1 Test-tube stand with at least 12 holes.
- 1 Nest of 3 or 4 small-sized beakers.
- 1 Length of glass rod.
- \*1 Small porcelain crucible, about  $1\frac{1}{4}$  inch across, and lid.
- 1 Strip of platinum foil, 2 inches by 1 inch.
- 2 Pieces of platinum wire,<sup>1</sup> each  $1\frac{1}{2}$  to 2 inches long.
- 1 Black's blowpipe.
- 1 Pipe-clay triangle, 2 inches in the side.
- \*1 Pair of brass crucible-tongs.
- 1 Large flask for wash-bottle, 18 oz. capacity, and from 1 to  $1\frac{1}{4}$  inch across the neck.
- \*1 Wooden filtering-stand.
- \*1 Tin filter-dryer.
- 1 Small wicker-basket for draining test-tubes and other glass and porcelain apparatus after they have been washed. Little toilet baskets, 12 inches in length by  $5\frac{1}{2}$  and  $4\frac{1}{2}$  inches high, serve well.

*Note.*—For the experiments with gases the student will also require :

\*A pneumatic trough, or earthenware pan as a substitute for it (see note, p. 23).

A small piece of candle.

A wax taper, or slips of wood.

A few sound corks of such a size as to fit test-tubes or small flasks.

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*Caution.*—In a laboratory where many students are working, it is best to mark at once each piece of apparatus with initials, number, or with some private mark, so as to be able to recognize it if mislaid. Glass, metal, or porcelain apparatus may be notched with the edge of the three-cornered file, or characters may be scratched upon it with the sharp points made by breaking off the tip of a three-cornered file. Wooden apparatus can be written upon with pen and ink, or scratched with the tip of a penknife.

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<sup>1</sup> Platinum wire containing Ba is not uncommon; it is known by giving a persistent green color to the Bunsen flame, and is useless for flame colorations.

## APPARATUS FOR GENERAL USE.

495. The following apparatus need not be purchased by each student, but should be kept in constant readiness for general use:

496. *An Indigo-prism.*—A hollow glass prism, having an extremely small angle at its extremity, with ground-glass stopper fitting water-tight into the neck, is purchased; this is to be very nearly filled with solution of indigo, and the stopper then tied in securely with fine copper wire. The indigo solution is made either by diluting a solution of indigo in strong sulphuric acid until it has the required intensity of color,<sup>1</sup> or by dissolving indigo-carmin in water; the liquid is then allowed to stand for several days to give time for any sediment which may form to settle completely, and when quite clear is decanted into the prism. In the thicker part of the prism the blue must be so intense as to arrest the passage of the light from a flame colored yellow with a sodium compound, and to cause the potassium flame coloration to appear crimson-red.

497. *Several Small Slips of Cobalt Glass.*—This glass is used for the same purpose as the indigo-prism, but the prism is to be preferred, more especially for the examination for Sr.

498. *Set of Cork-borers.*—These are used for perforating a cork into which a piece of glass tubing has to be inserted (8). Nests of borers containing the three or four smallest sizes will be sufficient.

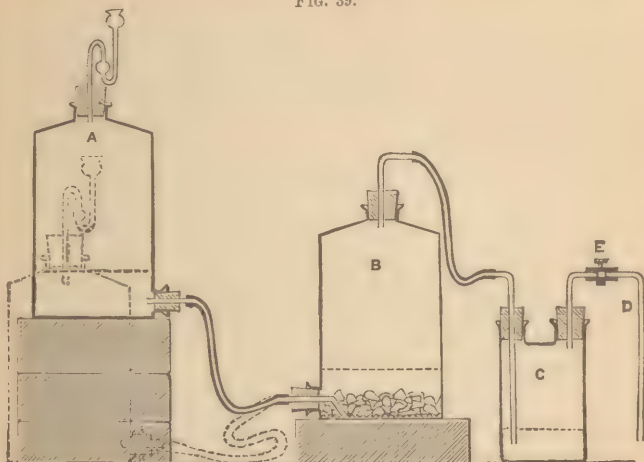
499. *Sulphuretted Hydrogen Apparatus.*—It is advisable to employ a large apparatus which will supply this gas to all who are working in the laboratory. The use of a small private apparatus by each student not only causes unnecessary waste of materials and time, but vitiates the air of the laboratory whilst it is being washed out.

Many forms of apparatus have been devised to supply the gas in a constant stream: probably the following, the

<sup>1</sup> The addition of the indigo solution to ten times its measure of acid will usually give the required shade.

simplicity, efficiency, and cheapness of which render it very satisfactory, will be found the most generally useful.

FIG. 39.



*Note.*—The level of the liquids in the vessels is shown by dotted lines; the vessel A when lowered from its stand is also shown in dotted outline. The whole is drawn in section.

**500. *Sulphuretted Hydrogen Apparatus.***—Two large bottles, A and B, with wide necks, and tubulures near the bottom, and of at least two quarts capacity, are fitted as shown in section in Fig. 39.<sup>1</sup> India-rubber stoppers should be used instead of corks, as the latter soon become sodden with acid and rotten, and also lose their elasticity and permit leakage. The vessel B is laid upon its side to prevent breaking the bottom, and lumps of ferrous sulphide are dropped into it: the cork is then inserted, the clamp at E being closed. The glass tube fixed in the lower tubulure of B should be bent downwards, so that its end nearly touches the bottom of the vessel. This drains the acid out of B to the lowest possible level when A is lowered. Strong commercial

<sup>1</sup> This apparatus may be purchased completely fitted from Messrs. Mottershead, of Manchester, and from most apparatus sellers.

hydrochloric acid<sup>1</sup> is poured into A, then an equal bulk of water is added, and the liquids are mixed by shaking the vessel.

When the gas is required, the vessel A is raised by being placed on a stand of suitable height, the acid runs into B, generates the gas by acting on the ferrous sulphide, and by the pressure of the liquid in A the gas is forced through a little water in the washing-bottle C, and thence through a bent tube at D into the liquid which is to be saturated with sulphuretted hydrogen.

When the flow of the gas is to be stopped, the screw-clamp on the india-rubber joint at E is tightened; by proper management of this screw-clamp the stream of gas can be either totally arrested or controlled to any required extent; this clamp must always be so regulated as to permit of as little waste of gas as possible whilst using the apparatus.

During working hours the vessel A should be kept raised, as shown in the figure; when laboratory work ceases it should be lowered to the position shown in dotted outline. The vessel B is always kept slightly raised by being placed on a wooden block or a brick, so as to encourage the flow of the last portions of acid out of it into A when A is lowered. When the acid is spent, it is easily poured out of A and replaced by fresh; lumps of ferrous sulphide are added as required through the neck of B. The removal of the spent acid and the cleansing of the apparatus should be performed in the open air, or at a sink in a cupboard provided with a good draught.

The neck of A may be kept stopped with a cork carrying a bent funnel whose bend is filled with oil or glycerin; this lessens the escape of gas dissolved in the acid, and tends to prevent the apparatus from causing a smell. If several students require to use the gas at the same time, the broad stopper of B is perforated and

<sup>1</sup> The use of  $\text{H}_2\text{SO}_4$  instead of  $\text{HCl}$  is objectionable, since  $\text{FeSO}_4$  crystallizes in the apparatus, impeding or preventing the action of the acid and its flow through the connecting tube; also, it does not produce such an easy and rapid evolution of the gas.



fitted with additional tubes and wash-bottles, or a system of distributing pipes or T-pieces connected with the tube from the cork in B may be employed.

An apparatus for private use may be fitted as shown in Fig. 40. The larger bottle contains pieces of ferrous sulphide upon which HCl, diluted with an equal measure of water, is poured through the thistle-funnel; the gas bubbles through a little water in the smaller bottle, and thence into the solution to be saturated.

FIG. 40.



The sulphuretted hydrogen apparatus should stand in a cupboard with a glass front and small doors, which is not used for any other purpose; the cupboard must be furnished with a flue in which a strong draught is created by an argand or ring gas-burner, made of fire-clay or steatite and not of metal; if the cupboard doors are kept closed as much as possible, and students when using the gas are careful to prevent its unnecessary escape, the atmosphere of the laboratory may be kept tolerably free from this badly smelling gas. The cupboard should have within it a drain into which are emptied the spent acid and washings of the apparatus.

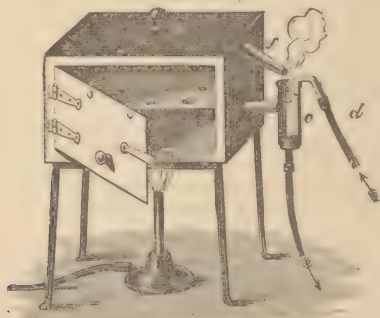
**500 a. Passing Sulphuretted Hydrogen into a Liquid.**—Each student should keep a bent glass tube (D, Figs. 39 and 40), made according to the directions in par. 9: when the gas has to be passed into a liquid, the shorter end of this tube is fitted into the india-rubber joint E, and the other end is passed nearly to the bottom of the liquid; on slightly opening the clamp E, a stream of the gas will bubble up through the liquid and may be regulated by the clamp; when the gas has passed for about five minutes the liquid will generally be saturated; if this is the case it will smell of the gas strongly after the air above the liquid has been blown out of the vessel and the vessel has been well shaken. Great care must be taken to close the clamp at E completely when the gas is stopped. The tube D must be thoroughly cleansed after use, employing a tobacco-pipe cleaner if necessary for its inside.

**501.** *A Small Agate Pestle and Mortar* (Fig. 32, p. 75).—This is required for powdering very hard substances, more particularly minerals. The substance must have been already broken into small fragments, and these are then crushed to powder by pressure and “trituration,”<sup>1</sup> until a powder is produced in which no particles or grains are felt when it is pressed or rubbed with the pestle or the finger; such a powder is commonly termed an “impalpable powder.” On no account must a substance be broken by placing it in the mortar and striking it blows with the pestle, as this is very liable to cause the fracture of the mortar.

**502.** *Several small leaden cups or a platinum crucible* should be kept in readiness for testing for F by paragraph (295) or (296). The leaden cups are easily made by beating out thick sheet lead into the required shape, the mouth being of such a size as to be readily covered by a watch-glass; the small leaden inkpots often employed in school-desks serve well for this purpose.

**503.** *A Steam-oven.*—This is a small oven of sheet

FIG. 41.



copper, heated to the temperature of boiling water ( $100^{\circ}\text{C.}$ ) by water contained in the space between the exterior of the oven and a copper casing which surrounds it (Fig. 41); the outer casing often has a circular opening cut in the top, covered by a lid when not in use,

<sup>1</sup> Rubbing round and round under the pestle.

which serves as a water-bath (504). The level of water in the jacket is maintained constant by a little contrivance shown in section at *c*: a small reservoir communicating by a lateral tube with the space between the oven and its jacket is constantly replenished by water which drops into it from the supply-tube (*d*); the overflow of this reservoir is a tube rising in its centre whose end terminates inside above the level of the lateral tube. The outlet for steam (*f*) may be turned downwards, so that any water formed by the condensation of the steam drops into the reservoir (*c*), or it may be made to communicate with the worm of the still (506), the escape steam being thus condensed into distilled water. The steam-oven should always be supplied with distilled water, as this prevents the formation of a troublesome incrustation in the interior. A vessel of distilled water may be connected with the oven by a siphon, having a bulb or vertical closed tube at its bend, to prevent the air boiled out from the water from stopping the action of the siphon; or the escape-pipe (*f*) may be turned upwards and connected with a long vertical or oblique tube, which, if the flame is small, will condense the escaping steam, and obviate the necessity of a constant supply of water.

The steam-oven is employed to drive off the moisture from solid substances which require to be dried at a gentle heat.

**504.** *Several Copper Water-baths.*—The water-bath consists of a hemispherical copper dish with its edges turned over inwards; a series of flat copper rings of gradually diminishing diameters are made to rest upon the edges of the bath or upon one another's edges, so that the opening at the top can be made as small as may be desired. The bath is about two-thirds filled with water, and is heated on a tripod-stand until the water boils, the excess of steam escaping by a small hole made just below the edge of the bath; the flame should be so regulated that the water is kept gently boiling. A small-sized saucepan is a homely substitute for the copper water-bath.

Any liquid requiring to be evaporated at a gentle heat is placed in an evaporating-basin upon this bath, its tem-

perature during evaporation cannot then exceed the temperature of boiling water ( $100^{\circ}$  C.).

The top of the water-oven is frequently made to serve as a water-bath, see (503). If the water-bath requires to be used for any considerable length of time, it may be supplied with water in the same way as the steam-oven (503).

**504 a.** The following cheap and simple device serves the purpose of both water-bath and steam-oven on a small scale. Two circular plates of sheet zinc are obtained,<sup>1</sup> about four inches in diameter, so as to cover the larger-sized porcelain dishes used by each student; in one of these a circular hole concentric with the edge of the plate and two and three-quarters inches in diameter is cut, in the other a similar hole is made one and a half inches across. These covers, when placed on one of the larger porcelain dishes, nearly filled with water and boiled by a lamp, convert it into a water-bath, a small dish containing the liquid to be evaporated being supported in the hole of the plates; small quantities of liquid may be evaporated or solid substances may be dried by placing them on a watch-glass supported on the smaller perforated plate.

In a large laboratory, however, steam-ovens and water-baths are usually kept constantly heated by steam or boiling water, and are used in common by all students. The steam from a large water-bath may advantageously be condensed to distilled water by connecting the escape-pipe of the bath with a long tube or the still-worm.

**505.** *Several Small Tubulated Flasks.*—The small flask shown in Fig. 38 (p. 150) is very convenient for the reactions described in pars. 260, 264, and 273. It is the form of apparatus best suited for the test for a chloride described in (260) because the  $K_2Cr_2O_7$  powder is not introduced through the same tube as the  $CrO_2Cl_2$  escapes by, and the risk of the mixture in the flask spirting into the delivery-tube is rendered very small. Its neck should be closed by an india-rubber or glass stopper.

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<sup>1</sup> Any working tinman will make them to order.

## DISTILLATION OF WATER.

As has been already shown (Ex. 31, p. 40) water ordinarily contains certain solid substances dissolved in it which render it in a chemical sense impure; such water is therefore unfit to be employed for the process of solution and washing, since any impurity thus introduced into a substance during analysis would be considered when detected to have been present in the original substance. The quantity of these impurities present in any particular water-supply will depend upon the nature of the soil with which the water has been in contact previous to its collection. The water supplied in some districts will be found when subjected to the tests given in [(526) Remark 41] to be almost perfectly pure; carefully collected rain-water will invariably yield no indication of dissolved impurity; the water supplied to the majority of laboratories will, however, be found to be unfit for analytical purposes, until it has been freed from the solid substances dissolved in it by being subjected to the process of distillation.

In most towns distilled water can be purchased, but it is preferable to distil in the laboratory or its immediate neighborhood all the water required for use. For this purpose the steam obtained either from a steam-boiler or from a copper still heated by a furnace or gas-burner, or from the water-baths and steam-ovens in the laboratory, is condensed by a tin worm-pipe immersed in a tub through which a constant stream of cold water runs.

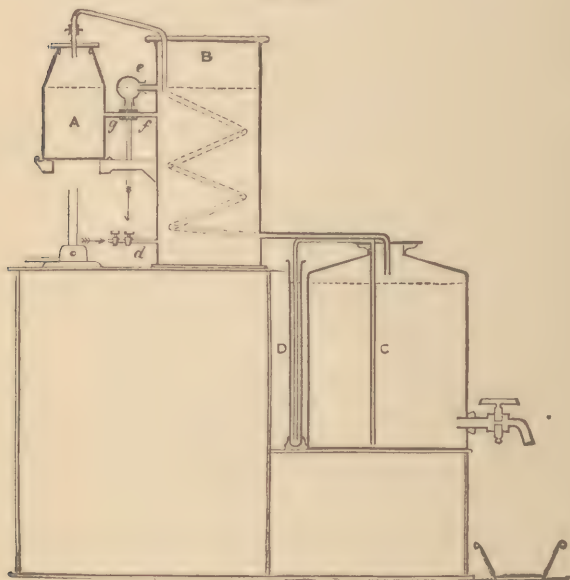
506. The following constant apparatus has proved most serviceable in the author's laboratory, and may be used wherever gas and water are laid on in a suitable way. Its advantage lies in the fact that the still is constantly supplied with the hottest portion of the water from the condenser through a lateral tube. When the apparatus has been properly fitted up and the supply adjusted, it requires no attention whatever except lighting and extinguishing the gas under the still, and turning the water-supply on and off when distillation is started and stopped; it is advisable occasionally to remove from the interior of the still, and from the supply-



tube connecting it with the condensing vessel, the deposit which accumulates by evaporation of the water.

The accompanying sketch (Fig. 42) renders a lengthened description of the apparatus unnecessary ; it represents the apparatus in section. A copper still (A) is heated by the flame of a large-sized Bunsen burner or by

FIG. 42.



a ring gas-burner, the steam passing off from the top of the still through a tin tube bent into a spiral form in the condensing-tub (B) which is made of copper or galvanized iron ; from this condenser the distilled water flows into a large stoneware vessel (C), with a tap below from which the water is drawn when required. A long siphon-tube (C D) serves as a gauge. The condensing-tub (B) has three tubes let into the side facing the still ; one of these (d), placed about an inch above the bottom of the vessel, is the inlet for cold water from a cistern whose water level must be higher than that maintained in A

and B; this level is marked by the single dotted line, and is kept constant by the overflow-tube *c*, which is connected with a pipe leading to a sink or drain. Just below this overflow-tube is a short tube (*f*), which is on a level with another (*g*), opening into the side of the still; by connecting these two tubes with an india-rubber joint, a supply of warm water from the upper part of the condenser is furnished to the still, keeping the level of water in it constant; a small glass jet drawn out from a piece of glass tubing is fitted into this connecting-tube, and has been found sufficient to prevent a too free circulation of water between the still and condenser. The still is supported on an iron ring, projecting as a bracket from the condenser. By having two taps in the inlet-tube (*d*), or by using two clamps on the india-rubber joint which connects it with the supply-pipe from the cistern, much time is economized, as the flow of water may be regulated once for all by one tap or clamp, the other being used only for stopping and starting the stream. The copper still should be furnished with a lid screwing upon its mouth for convenience in removing the deposit which collects within, and into this lid should be fastened a brass tube carrying a screw-union by which the tin condensing-pipe may be fastened steam-tight to the still. The wooden stand for the still and storing-jar is conveniently fitted with shelves and doors to serve as a cupboard. Such a copper still, 23 inches in circumference below and 8 inches in height, when filled to a height of 4 inches and heated by the largest-sized Bunsen burner, yields 2 liters of distilled water per hour.

In laboratories where a larger supply of distilled water is required, a copper still of several gallons capacity may be set in masonry and heated by a small furnace fed with coal or gas. The overflow from the still-tub should then pass into a small cistern whose overflow-pipe keeps its water surface level with that required in the still; and the still and cistern are connected by a tube bent downwards in its middle to prevent the passage of water from the still to the cistern.

For tests of purity see Remark 41 (526).

## RECOVERY OF THE METALS FROM SILVER AND PLATINUM RESIDUES.

When  $\text{AgNO}_3$  or  $\text{PtCl}_4$  has been added to a solution the liquid is not to be thrown into the sink.

**507. Silver Residues.**—If  $\text{AgNO}_3$  has been added to a liquid it must be emptied into a vessel,<sup>1</sup> labelled “Silver Residues,” containing strong  $\text{HCl}$ , which precipitates  $\text{AgCl}$ . When the vessel is full, the  $\text{AgCl}$  is allowed to settle, and the liquid decanted from the  $\text{AgCl}$ ; more  $\text{HCl}$  is then poured in, and the vessel is again ready for use. When a sufficiently large quantity of  $\text{AgCl}$  has been formed, let it settle, decant off the liquid, and wash the precipitate well by decantation; pour it upon a filter, and dry upon the filter. One of the two following methods may then be employed to obtain metallic  $\text{Ag}$  from the  $\text{AgCl}$ :

1. Mix the  $\text{AgCl}$  with twice its weight of a mixture in equal proportions by weight of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ ; place this in a clay crucible of such a size that the mixture only half fills it, and heat in a furnace until the mass becomes liquid; maintain it in a fused condition for about five or ten minutes, remove the crucible, and tap its bottom several times gently upon a brick to cause the fused particles of  $\text{Ag}$  to unite. Allow the crucible to cool, break it up, and wash the button of  $\text{Ag}$ , which will be found at the bottom, until it is quite free from adhering salts.

This button is then dissolved by heating it in a flask with pure strong  $\text{HNO}_3$  previously diluted with about half its measure of water; the solution is evaporated to dryness, the residue dissolved in a little water and once more evaporated to complete dryness. The  $\text{AgNO}_3$  is then dissolved in the right proportion of water to furnish reagent No. 48 (525).

2. A readier method for decomposing the  $\text{AgCl}$  consists in placing it in a dish with a little water acidified

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<sup>1</sup> Most conveniently a large bottle, with a funnel in its neck.

with dilute  $\text{H}_2\text{SO}_4$ , and laying upon the  $\text{AgCl}$  some strips of  $\text{Zn}$  free from  $\text{Pb}$ ; after some hours the  $\text{Ag}$  will be separated as a black spongy mass. This is well washed by decantation with hot dilute  $\text{H}_2\text{SO}_4$ , and then washed also by decantation with boiling distilled water till free from the  $\text{H}_2\text{SO}_4$ ; the  $\text{Ag}$  is dissolved in  $\text{HNO}_3$  as directed in the first process, the solution evaporated to dryness, and the  $\text{AgNO}_3$  used for preparing the reagent. Any residue insoluble in  $\text{HNO}_3$  will be unreduced  $\text{AgCl}$ ; this may be filtered off and added to the silver residues for subsequent reduction.

508. *Platinum Residues*.—Liquids to which  $\text{PtCl}_4$  has been added are poured into a vessel<sup>1</sup> labelled “Platinum Residues;” when a sufficient quantity has been obtained the liquid and precipitate are poured into a porcelain dish, evaporated to dryness, and heated strongly for some time; as soon as the dish is cool the residue is boiled with water, which is decanted, and upon the residue some solution of oxalic acid is poured; this is evaporated to dryness and the residue strongly ignited. The residue of metallic  $\text{Pt}$  is once more washed with boiling water, and is then dissolved by heating it with  $\text{HCl}$  to which one-third its measure of  $\text{HNO}_3$  has been added; the solution is evaporated to dryness, the last part of the process being performed over a water-bath.  $\text{HCl}$  is then poured in, and it is once more evaporated to dryness and heated for some time on the water-bath; this residue when dissolved in water forms the reagent No. 28 (525). Any waste scraps of platinum foil and wire should be carefully preserved, and after having been cleansed by boiling them with  $\text{HNO}_3$  and washing well with water, they may be dissolved in  $\text{HCl}$  and  $\text{HNO}_3$  and solution of  $\text{PtCl}_4$  prepared as is described above.

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<sup>1</sup> Conveniently a large glass bottle, with a funnel in its neck.

## DIRECTIONS FOR PREPARATION OF REAGENTS.

*Note.*—The reagents required for chemical analysis are much more readily obtained at the present time than they were in former years. They can usually be purchased in a pure state, and therefore processes of preparation, which formerly of necessity occupied a large portion of Manuals of Practical Chemistry, are here omitted. It will be found usually more economical to purchase pure chemicals than to prepare them.

**509.** Many reagents are required in a dissolved or diluted state; it is a matter of much importance that these solutions should be made of a proper strength, and that the methods of preparing them should be as rapid and simple as possible.

The strength of the solutions is chosen somewhat arbitrarily; indeed, the strength of a solution may be varied with advantage according to the different purposes for which the reagent is to be employed. It is found, however, that in practice a solution of one strength may usually be made to serve all analytical purposes. The proportions of liquid or solid to be mixed with or dissolved in a certain quantity of water, which are given hereafter, are those (or very nearly those) recommended in standard works on analysis. It is not intended, however, to assert that they are for *all* purposes the best, but merely that they are generally suitable.

**510.** A good and economical store-bottle for liquid reagents is the "Winchester quart" bottle, a stock of which generally accumulates in a laboratory, being continually introduced filled with strong acids. The following methods of filling these have been found simple and easy of execution.

The process of preparing solutions divides itself naturally into the "dilution of liquids" (511), and the "solution of solids" (512).

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### 511. DILUTION OF LIQUIDS.

In the following lists the proportions by measure are stated in which the liquid and distilled water are to be



mixed; these proportions are roughly, but sufficiently accurately, obtained by measuring with a foot-rule the height of the bottle outside from the bottom to the projecting ridge at the shoulder, then dividing this height in the required proportions, and marking the point of division by a line scratched upon the bottle with a three-cornered file. Thus dilute  $\text{HCl}$  (No. 2, 524) is made by mixing strong  $\text{HCl}$  with three times its measure of water; supposing, then, the measured height of the "Winchester" to the shoulder to be 8 inches, a file-mark is made 2 inches from the bottom, and on filling the bottle to this mark with strong  $\text{HCl}$ , then up to the shoulder with distilled water, stoppering and shaking up, a dilute acid of the required strength is obtained. This method serves for numbers 2, 3, 4, 6, and 7 (524). For the preparation of No. 1 see column of remarks in the same paragraph.

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## 512. SOLUTION OF SOLIDS.

For dissolving solids two methods are here described; the former (514) is useful when the solution has to be rapidly prepared; the latter (515) requires less attention, and may be used when the solution is not required at once.

513. Against each reagent prepared from a solid there is placed in paragraph (524) a number, signifying the number of grams (see 560 *et seq.*) to be dissolved in one Winchester quart of water, and in all the lists will be found the proportion by weight of solid to water. The former number is obtained from the proportion stated in the next column, by considering that an average-sized "Winchester," filled an inch above the ridge round its shoulder, holds about 2400 cc., and since each cc. (560 *et seq.*) of water weighs approximately 1 gram, we have at once the weight of water (2400 grams) contained in the bottle, from knowing its capacity; and, the weight of water being known, the weight of solid to be dissolved in it is readily calculated from the proportion given.<sup>1</sup>

Thus the proper strength of  $\text{AmCl}$  solution (No. 5, 524) is 1 of solid  $\text{AmCl}$  dissolved in 8 of water, as shown in the fifth column, or a given

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<sup>1</sup> This method may also be employed when smaller quantities of the reagent are to be prepared. Measure the number of cc. required to fill the bottle, count the number as grams, and calculate the proportion of solid required as above.

weight of water must have dissolved in it  $\frac{1}{4}$ th its weight of  $\text{AmCl}$ ; since a "Winchester" holds 2400 grams of water, we must then dissolve  $2\frac{1}{4} \times 2400 = 300$  grams of  $\text{AmCl}$  in it to obtain a solution of proper strength.

**514. METHOD I.**—Weigh out the required quantity of the solid substance, dissolve by heating it with distilled water in a large-sized porcelain dish placed on a tripod-stand over a rose-burner; this solution would often crystallize on cooling, hence it should be at once poured into some cold distilled water contained in a large beaker marked to show the quantity of liquid required to fill the "Winchester." Whilst pouring off the liquid press a wet glass rod, held vertically, against the lip of the dish, and let the bottom of the dish touch the inside of the top of the beaker. These directions will, with proper care, prevent the liquid from running down outside the beaker. Dilute this up to the "Winchester" mark with distilled water, stir well, and if turbid let stand covered from dust until clear; then pour off into the store-bottle, carefully leaving the sediment behind. If the liquid is wanted in haste, it may be filtered into the bottle. The coarse brown French filter-paper is useful for this purpose, being strong and porous. It is best to filter the liquid before diluting it to the full extent, as the quantity to be passed through the filter is thus lessened and time economized.

The above method is of general application in the solution of solids.

**515. METHOD II.**—The following method is advantageous, because the process of solution once started proceeds continuously without further attention. It depends on the fact that the specific gravity of water becomes higher the greater the quantity of solid dissolved in it; hence if the solid is immersed in the water, and supported near the surface, a circulation of the liquid is produced by the constant sinking of the water which has been in contact with the solid, and by dissolving some of it has increased in specific gravity, this being replaced by the comparatively lighter liquid from below. The circulation of water over the solid gradually dissolves it

without the use of heat, and without requiring any attention after the process has once been started.

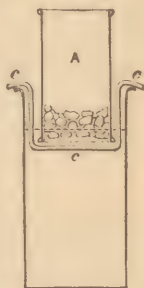
A glass cylinder (A, Fig. 43) open at both ends, has one end covered with a piece of muslin, shown by a fine dotted line, which is fastened on by an india-rubber ring, embracing its edges: this cylinder, with a muslin bottom, is supported in a large beaker by means of two pieces of glass rod or tube, bent as shown at *c c c*; the cylinder stands at such a height that the muslin bottom is about two inches below the mark made on the beaker to show the Winchester quart measure. Distilled water is then poured into the beaker until it buries the muslin to the depth of about half an inch; the weighed substance, best in small pieces, is placed in the cylinder, and the whole allowed to stand until the solid has been dissolved; with large quantities of substance this will usually require several hours, with smaller quantities about twenty minutes or half an hour.

The processes of solution and filtration are performed simultaneously by laying a piece of filter-paper upon the muslin before fastening it on the cylinder; the filter-paper will retard the process, but the coarse gray kind referred to above will do so least.

Perhaps the most advantageous way of using this process, especially for dissolving large quantities of substance, is to start it over night; the solution will then be completed by the morning. In this case the filter-paper will be unnecessary, as any fine particles which have passed through the muslin will have settled, and the liquid can be decanted from them.

It must be borne in mind that the solution of many salts in water, especially such salts as contain water of crystallization, increases the volume of the water; hence the quantity of water placed in the beaker must be less than the Winchester quart measure, and the liquid is made up to the required volume, if necessary, after solution has been effected.

FIG. 43.



As a convenient substitute for the glass cylinder, A, with muslin bottom, an earthenware colander may be employed (Fig. 43 a), filtration being effected when necessary by laying a piece of filter-paper inside the colander before placing in it the fragments of the substance. Should the beaker be able to contain more than the Winchester quart of water, a stoppered bottle of suitable size may be immersed in it to raise the water-level sufficiently to reach the substance.

FIG. 43 a.



#### PREPARATION OF SOLUTIONS REQUIRED FOR TRYING THE REACTION OF METALS AND ACID-RADICALS, SECTION IV.

**516.** The solutions required for trying these reactions should be prepared of a strength suited to yield them in a characteristic manner; it is therefore advisable that solutions of the requisite strength should be kept in readiness, since, if the student has to dissolve some of the solid substance himself, he is liable not to obtain satisfactory results, either because his solution is made inconveniently strong, or because it is too dilute. The plan of keeping these solutions in stock is also recommended by the consideration that it economizes the student's time and tends to prevent waste of chemicals.

**517.** In paragraphs (529) and (530) are lists of the solutions which are required for the complete series of reactions in Section IV: the first column gives the number, the second the name, and the third the formula of each substance; in the fourth is stated the number of grams which are to be dissolved in one Winchester quart of water or acid; in the fifth column the proportion by weight of solid to water, from which the number in column 4 was derived; and in the sixth column will be found special remarks relating to the preparation of particular solutions. The general methods of preparing

solutions have already been given in paragraphs (514) and (515).

Pure solid chemicals are almost invariably sold in the crystalline condition, since they have been as a rule purified by the process of crystallization. The weights given below are therefore weights of the crystalline substance; in a few cases the substance was weighed in the uncrystalline condition—these are marked by an (*a*) placed after the name in the first column, signifying “amorphous.” Directions for labelling the store-bottles of these solutions will be found in paragraphs (522) and (523).

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## LIST OF THE REAGENTS.

**518.** Paragraphs (524), (525), and (526) contain lists of the reagents, solid and in solution, which should be kept in readiness in the laboratory; they are dissolved in distilled water unless it is otherwise stated.

The reagents are here divided into two classes. The first (524) being in constant use and comparatively inexpensive, should be contained in small bottles placed above each working bench, or one complete set should be provided for the use of each student. The second class (525, 526) are less frequently required, or are of a more costly nature, and one set may be placed in an accessible part of the laboratory for the use of many students.

**519.** Each reagent is numbered in the following lists; this number is a convenient means of reference and also serves to keep the reagent bottles always standing in the same order, which much facilitates finding any bottle when wanted; the student is recommended to keep his bottles arranged in the order indicated by these numbers. The full name and chemical formula accompany each number, and every label in the laboratory should carry legibly the number, name, and formula of the reagent it contains.

**520.** In the last column of each list are placed remarks as to the preparation and the condition of the re-



agent. The numbers found in the last column but one express the strength of the solution of the reagent if a liquid, by stating the proportion of the strong liquid or solid as purchased to the water with which it is mixed or in which it is dissolved, the proportion being expressed as a ratio in which the water always stands last; in the case of liquids the numbers express proportion by measure (m.), in the case of solids the proportion by weight (w.). A number is also placed in the fourth column opposite each reagent prepared by dissolving a solid substance, which denotes the weight in grams of the solid to be dissolved in a Winchester quart bottle of water.

Thus No. 2 (524), hydrochloric acid, is prepared by mixing strong  $\text{HCl}$  with 3 times its measure of distilled water. No. 5, ammonium chloride, is made by dissolving solid  $\text{AmCl}$  in 8 times its weight of water, or by dissolving 300 grams of solid  $\text{AmCl}$  in one Winchester quart of water. Full descriptions are given in paragraphs (511), (514), and (515) of the methods used for making these solutions.

**521.** The special reagents which stand on shelves above the bench are kept in small bottles; the solids, Nos. 18–21 (524), in 4-oz. wide-mouthed stoppered bottles, which are filled when necessary from the store-jars (stone-ware jars with ground clasp-covers),<sup>1</sup> the liquids (Nos. 1–8) in narrow-necked 6-oz. bottles, and (Nos. 9–17) in 4-oz. bottles supplied from the Winchester quart bottles in which the store-solutions are kept. The general reagents (525, 526) should be kept in bottles of not less than 12 oz. capacity.

**522. Labelling.**—Bottles intended to contain strong acids or alkalies should have labels etched upon the glass; such bottles are easily obtained; an ordinary paper label, however, protected by paraffin varnish, which is applied according to the directions given below (523), will last for a considerable length of time.

The paper labels required for reagents and store-bot-

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<sup>1</sup> Powdered solids are conveniently removed from large store-jars by means of wooden spoons.

tles are most conveniently kept ready gummed in the form of sheets either separate or stitched together into the form of a book. They must be stored in a dry place. They should bear in bold legible type at least the full name and formula of the substance, the number, if not already printed, being written upon each.<sup>1</sup> Great care should be bestowed on making the moistened label adhere over its whole surface by gentle pressure with a clean cloth.

Names or formulæ painted upon the clean glass with "Brunswick black" paint are very permanent, resisting ordinary wear and the action of chemicals perfectly.

**523. Varnishing Labels.**—It is advisable to varnish each paper label, which is intended to be permanent, as soon as it is perfectly dry; the label is thus protected against being soiled or wetted. The ordinary process consists in first sizing the label by brushing over it a solution of isinglass in water, and then, as soon as this has perfectly dried, applying a thin coat of label varnish; the bottle must not be used until this varnish is quite hard.

A much more simple process of varnishing consists in melting some solid paraffin, which must not be heated so strongly as to cause it to emit vapor, and brushing this rapidly over the dry label with an ordinary varnishing brush; after a little practice a uniform film can be applied which does not soak into the paper, hardens immediately, and resists the action of water, acids, and alkalis. The chief precaution to be observed is to heat the paraffin as little as possible above its melting-point, as, if it is too hot, it greases the paper.

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<sup>1</sup> A book of labels ("A Series of Chemical Labels for use in Laboratories") is sold by Messrs. Mottershead, of Manchester, which contains the name of each substance in full, printed in clear type, space being left to insert formula and number.

Messrs. Mottershead also supply gummed sheets of labels, printed especially for use with this book, containing all the numbers, names, and formulæ in the lists in pars. 524, 525, 526, 529, 530, 531, and 532.

## 524. REAGENTS REQUIRED

1. Reference number.	2. Name. [The numbers in brackets refer to marks corre- spondingly numbered in the sixth column.]	3. Formula.
<b>Liquids.</b>		
1.	Sulphuric acid <sup>(1)</sup> .....	H <sub>2</sub> SO <sub>4</sub> .....
2.	Hydrochloric acid <sup>(2)</sup> .....	HCl.....
3.	Nitric acid <sup>(3)</sup> .....	HNO <sub>3</sub> .....
4.	Acetic acid <sup>(4)</sup> .....	{ HA. or HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> } .....
5.	Ammonium chloride <sup>(5)</sup> .....	NH <sub>4</sub> Cl .....
6.	Ammonia, or Ammonium hydrate <sup>(6)</sup> .....	NH <sub>4</sub> HO.....
7.	Ammonium sulphide <sup>(7)</sup> .....	(NH <sub>4</sub> ) <sub>2</sub> S.....
8.	Ammonium carbonate <sup>(8)</sup> .....	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> .....
9.	Ammonium oxalate.....	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .2H <sub>2</sub> O .....
10.	Potash, or Potassium hydrate .....	KHO.....
11.	Potassium chromate.....	K <sub>2</sub> CrO <sub>4</sub> .....
12.	Potassium ferrocyanide .....	K <sub>4</sub> FeCy <sub>6</sub> .3H <sub>2</sub> O.....
13.	<sup>1</sup> Potassium ferricyanide <sup>(9)</sup> .....	K <sub>3</sub> Fe <sub>2</sub> Cy <sub>12</sub> .....
14.	{ <sup>2</sup> Sodium phosphate <sup>(10)</sup> , or Hydric disodic phosphate, or Hydrogen disodium phosphate, }	Na <sub>2</sub> HPO <sub>4</sub> .12H <sub>2</sub> O.....
15.	Sodium carbonate.....	Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O. crystals
16.	Calcium sulphate.....	CaSO <sub>4</sub> .....
17.	Barium chloride.....	BaCl <sub>2</sub> .2H <sub>2</sub> O.....
<b>Solids.</b>		
18.	Sodium carbonate <sup>(11)</sup> .....	Na <sub>2</sub> CO <sub>3</sub> .....
19.	Borax <sup>(12)</sup> .....	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .....
20.	Potassium chlorate.....	KClO <sub>3</sub> .....
21.	Test-papers.....	.....

<sup>1</sup> This reagent undergoes decomposition by exposure to light and must not be kept near a<sup>2</sup> Hydrogen sodium ammonium phosphate, NaAmHPO<sub>4</sub> solution serves better for precipi-  
or Na<sub>2</sub>HPO<sub>4</sub>.

## FOR EACH BENCH.

4. Weight of solid in grams to be dis- solved in one "Win- chester" of water.	5. Proportion of solid by weight (w.) and liquid by measure (m.) to water.	6. [The small numbers refer to corresponding numbers in the second column.]
.....	1 : 5 m.	1. Pure strong $H_2SO_4$ must be poured in the proper proportion into water contained in a large thin beaker or an earthen jar, constantly stirring the water all the time; the right proportions are obtained by measurement of the height of the vessel (511). The hot liquid is cooled by immersing the vessel in cold water, and is then poured into the store-bottle. If the acid is pure, no white precipitate ( $PbSO_4$ ) forms on dilution.
.....	1 : 3 "	2. Must be colorless, and give after dilution no precipitate with either $BaCl_2$ or $H_2S$ .
.....	1 : 3 "	3. Must give no precipitate after dilution, with $BaCl_2$ or $AgNO_3$ added to separate portions.
.....	2 : 1 "	4. Must give no precipitate with $BaCl_2$ .
300	1 : 8 w.	5. Must give no precipitate or coloration with $Am_2S$ .
.....	1 : 3 m.	6. Must give only a very slight precipitate with lime-water, no coloration with $Am_2S$ , and separate portions acidified with $HNO_3$ must give no precipitates with $BaCl_2$ and $AgNO_3$ . "Liquor ammoniæ fortissima," of $880^\circ$ specific gravity, is bought.
.....	1 : 1 "	7. Must be yellow, and give with acids $H_2S$ and a white precipitate of S; it must give no precipitate with solutions of Ca or Mg salts.
400	1 : 5 w.	8. The solid $Am_2CO_3$ is dissolved by being heated with water in a porcelain dish (514); in diluting, one-fourth of the "Winchester" must be filled with strong $AmHO$ .
100	1 : 24 "	9. Must give no blue precipitate with $Fe_2Cl_6$ solution.
300	1 : 8 "	10. Must yield no precipitate with $AmHO$ .
200	1 : 12 "	11. Dry finely powdered solid. It must, after having been dissolved in excess of $HNO_3$ , give no precipitate with $BaCl_2$ or $AgNO_3$ , or $AmHMoO_4$ (277), and if evaporated with excess of $HCl$ must leave no residue insoluble in dilute $HCl$ (290 a).
200	1 : 12 "	12. The borax is best dried by heating in a platinum or porcelain dish until after melting it has again become solid; this solid mass is then finely powdered in a mortar and kept in a stoppered bottle.
200	1 : 12 "	
600	1 : 4 "	
Saturated solution (527).	1 : 12 "	
200		
In small crystals.		
Blue and red litmus and turmeric papers in small strips.		

window.

tation of Mg than does  $Na_2HPO_4$  solution; it is prepared of the strength given the above

## 525.—REAGENTS FOR GENERAL USE.

*Note.*—Except in large laboratories it will be unnecessary to keep these in the laboratory may be made up to the right strength as soon as they are

Reference number.	2. Name. [The small numbers in brackets refer to remarks correspondingly numbered in the fifth column.]	3. Formula.
25	Sulphuric acid <sup>(17)</sup> .....	H <sub>2</sub> SO <sub>4</sub> .....
26	Hydrochloric acid <sup>(2)</sup> <sup>1</sup> .....	HCl.....
27	Nitric acid <sup>(2)</sup> <sup>1</sup> .....	HNO <sub>3</sub> .....
28	<sup>2</sup> Platinum chloride.....	PtCl <sub>4</sub> .....
29	Alcohol, Rectified spirit <sup>(18)</sup> .....	C <sub>2</sub> H <sub>5</sub> O.....
30	Tartaric acid <sup>(19)</sup> .....	H <sub>2</sub> T or H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> .....
31	Acid sodium tartrate, Hydric sodic tartrate <sup>(20)</sup> .....	{ NaHT.H <sub>2</sub> O NaHC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> .H <sub>2</sub> O }
32	Slaked lime <sup>(21)</sup> .....	Ca HO.....
33	Acetic acid <sup>(1)</sup> <sup>1</sup> .....	HA or HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....
34	Cobalt nitrate <sup>(22)</sup> .....	Co NO <sub>3</sub> 2 6H <sub>2</sub> O.....
35	Hydrofluosilicic acid <sup>(24)</sup> .....	H <sub>2</sub> SiF <sub>6</sub> .....
36	{ Sulphuretted hydrogen solution } <sup>(23)</sup> .....	H <sub>2</sub> S solution.....
	{ Hydrogen sulphide }	
37	Oxalic acid.....	{ H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .2H <sub>2</sub> O } { H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .2H <sub>2</sub> O }.....
38	Potassium sulphocyanide.....	KCyS.....
39	Potassium nitrate.....	KNO <sub>3</sub> .....
40	Lead acetate <sup>(25)</sup> .....	{ PbA <sub>2</sub> .3H <sub>2</sub> O Ph(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> .3H <sub>2</sub> O }.....
41	Sodium acetate.....	{ NaA.3H <sub>2</sub> O NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .3H <sub>2</sub> O }.....
42	Potassium cyanide <sup>(26)</sup> .....	KCy or KCN.....
43	Bromine water <sup>(27)</sup> <sup>2</sup> .....	Br-water
44	Stannous chloride <sup>(28)</sup> .....	SnCl <sub>2</sub> .2H <sub>2</sub> O.....
45	Copper <sup>(29)</sup> .....	Cu
46	Zinc <sup>(30)</sup> .....	Zn
47	Steel <sup>(31)</sup> .....	Fe
48	Silver nitrate.....	AgNO <sub>3</sub> .....
49	Sulphurous acid.....	H <sub>2</sub> SO <sub>3</sub> .....
50	Copper sulphate.....	CuSO <sub>4</sub> .5H <sub>2</sub> O.....
51	Magnesium sulphate.....	MgSO <sub>4</sub> .7H <sub>2</sub> O.....
52	Mercuric chloride.....	HgCl <sub>2</sub> .....
53	Gold chloride.....	AuCl <sub>3</sub> .....

<sup>1</sup> See last column on the preceding page.

<sup>2</sup> Must be used in very small quantity only, being an expensive reagent.

<sup>3</sup> Sodium hypochlorite (Na<sub>2</sub>Cl<sub>2</sub>O), the "Liquor Sodæ Chlorinatæ" of commerce may be used, but does not keep well.



## FOR THE DETECTION OF METALS.

agents in store in quantity. The 12-oz. bottles in which they are contained empty by the proportions stated below in column 4.

4. Proportion by weight of solid to water, and weight in grams for a 12-oz. bottle in square brackets.	5. Remarks. [The numbers in this column refer to those in brackets in the second column.]
.....Strong pure.	17. Must be colorless and form no brown ring when poured below some $\text{FeSO}_4$ solution (247).
....." "	18. Strong rectified methylated spirit, which must leave no residue on evaporation, and remain clear on dilution.
....." "	19. The solution should be mixed immediately after preparation with several drops of carbolic acid to prevent a vegetable growth forming in it; or better still some crystallized $\text{H}_2\text{T}$ should be dissolved when wanted.
.....1 : 30 [15 grams].	20. Dissolve 10 grams of $\text{H}_2\text{T}$ in 100 cc. <sup>1</sup> of water, divide this solution into equal parts, exactly neutralize (35) one part by heating it nearly to boiling and stirring in solid $\text{Na}_2\text{CO}_3$ in powder; add to this the other part, cool and dilute to 150 cc. A few drops of carbolic acid should be added to the solution.
.....Strong.	21. Pieces of freshly burnt lime are placed on a plate, and water is poured upon them until they begin to appear moist on their surface; the superfluous water is then drained off, and as soon as the lime has crumbled to powder, the powder is placed in a broad-mouthed stoppered bottle.
.....1 : 10 [15 grams].	22. The bottle should be closed with a loosely fitting india-rubber stopper, perforated, and with a glass tube passed through it and dipping into the solution; when a drop of the solution is required, the upper end of the glass tube is closed by the finger, and a drop is delivered from the opposite end by slightly relaxing the pressure of the finger.
.....Solid.	23. The solution must give no precipitate with $\text{Sr}(\text{NO}_3)_2$ solution.
.....Strong.	24. This solution must not darken on adding $\text{AmH}_2\text{O}$ .
.....1 : 12 [40 grams].	25. A little HA must be added to this solution to make it clear.
.....See (528, 4).	26. Solution of KCy is made (1 : 12); it decomposes so readily that the solution is best made immediately before use by heating a small piece of solid KCy with distilled water.
.....See (528, 1).	27. A few drops of Br dissolved by well shaking with water.
.....1 : 12 [40 grams].	28. Crystals of $\text{SnCl}_2$ should be dissolved by heating them with water containing some HCl; the solution should be kept in a well-stoppered bottle containing pieces of granulated or block tin.
.....1 : 100 [5 grams].	29. In strips cut from thin copper sheet.
.....Solid.	30. In strips or rods, or granulated; it must be proved to be free from As by (181, 182, or 183).
.....1 : 12 [40 grams].	31. Common knitting-needles broken into short lengths, and kept in a bottle containing pieces of quicklime to prevent rusting.
.....1 : 20 [30 grams].	
.....See (528, 2).	
.....1 : 12 [40 grams].	
.....1 : 12 [40 grams].	
.....1 : 20 [30 grams].	
.....1 : 30 [15 grams].	

<sup>1</sup> cc. is the contraction for cubic centimeter. See weights and measures (560).

## 526.—REAGENTS FOR GENERAL USE,

Refer to note under

1.	2.	3.
Reference number.	Name. [The small numbers in brackets refer to corresponding numbers in the fifth column.]	Formula.
57	Lime-water.....	$\text{CaHO}_2$ .....
58	Lead acetate in potash <sup>(32)</sup> .....	$\text{PbA}_2 + \text{KHO}$
59	Potassium dichromate.....	$\text{K}_2\text{Cr}_2\text{O}_7$ .....
60	Chlorine-water.....	Cl solution.....
61	Ferric chloride <sup>(33)</sup> .....	$\text{Fe}_2\text{Cl}_6$ .....
62	Ferrous sulphate <sup>(34)</sup> .....	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .....
63	Potassium iodide.....	KI.....
64	Starch <sup>(35)</sup> .....	.....
65	Indigo solution <sup>(36)</sup> .....	.....
66	Manganese dioxide <sup>37</sup> .....	$\text{MnO}_2$ .....
67	Potassium dichromate <sup>(38)</sup> .....	$\text{K}_2\text{Cr}_2\text{O}_7$ .....
68	Ether (methylated).....	$(\text{C}_2\text{H}_5)_2\text{O}$
69	Carbon disulphide.....	$\text{CS}_2$
70	Potassium nitrite <sup>(39)</sup> .....	$\text{KNO}_2$ .....
71	Nitrogen tetroxide solution.....	$\text{N}_2\text{O}_4$ solution.....
72	Ammonium molybdate <sup>(40)</sup> .....	$(\text{NH}_4)\text{HMoO}_4$
73	Calcium fluoride.....	$\text{CaF}_2$ .....
74	Potassium disulphate.....	$\text{KHSO}_4$ .....
75	{ Microcosmic salt, or Hydric ammonic sodic phosphate } <sup>(40 a)</sup> .....	$\text{NaAmHPO}_4 \cdot 4\text{H}_2\text{O}$ .....
76	Wax, or paraffin.....	.....
77	Calcium chloride.....	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (crystals)...
78	Potassium chloride.....	KCl.....
79	Marble.....	$\text{CaCO}_3$ .....
80 <sup>1</sup>	Distilled water <sup>(41)</sup> .....	$\text{H}_2\text{O}$ .....
81	Pure sodium hydrate <sup>(42)</sup> , pure soda.....	$\text{NaHO}$ .....
82	Fusion mixture <sup>(43)</sup> .....	$\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ .....
83	Barium carbonate <sup>(44)</sup> .....	$\text{BaCO}_3$ .....
84	Solution of sodium acetate in dilute acetic acid <sup>(45)</sup> .....	$\text{NaA} + \text{HA}$ .....
85	Sodium nitrate <sup>(46)</sup> (solid).....	$\text{NaNO}_3$ .....
86	Silica, or finely powdered white sand. (See 548, 4)	$\text{SiO}_2$ .....
87	Hydrofluoric acid <sup>(47)</sup> .....	HF.....
88	Barium hydrate (in crystals).....	$\text{BaHO}_2 \cdot 8\text{H}_2\text{O}$ .....
89	Zinc sulphate. (See No. III.).....	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .....

<sup>1</sup> Nos. 80-89 are certain special

## FOR THE DETECTION OF ACID-RADICLES.

the heading of (525).

4. Proportion by weight of solid to water; and weight in grams for a 12-oz. bottle in square brackets.	5. Remarks. [The numbers in this column refer to corresponding numbers in the second column.]
.....See (527).	
.....1 : 24 [20 grams].	32. To some of the $\text{Pb.A}_2$ solution (No. 40) $\text{KHO}$ solution is added until, on warming, the precipitate at first formed is just redissolved; paper dipped into this liquid is a very delicate test for $\text{H}_2\text{S}$ (236).
.....See (528, 5).	33. The solution should not contain any free acid: to remove acid $\text{AmHO}$ is added until the further addition of a single drop gives a reddish-brown precipitate of $\text{Fe}_2\text{HO}_6$ in the solution.
.....1 : 24 [20 grams].	34. $\text{FeSO}_4$ solution rapidly oxidizes in the air, hence the $\text{FeSO}_4$ should be kept in the solid state as small green crystals, which should not show a yellow coating in any part: these are dissolved when required by crushing and shaking with cold water.
.....Solid.	35. Starch solution rapidly changes; it is best therefore to keep the starch as a powder. Starch solution is made by stirring 2 grams of this powder, which has been made into a paste with 10 cc. of cold water, into 100 cc. of boiling water and cooling.
.....1 : 60 [8 grams].	36. Made by dissolving indigo carmine in water.
.....Solid.	37. Should be kept in fine powder; it must not evolve $\text{Cl}$ or $\text{CO}_2$ when warmed with strong $\text{H}_2\text{SO}_4$ .
.....Solid.	38. In small pieces, or in powder.
.....1 : 24 [20 grams].	39. The solution is prone to change, and should be made in small quantity only; it must evolve copious red fumes when mixed with $\text{H}_2\text{SO}_4$ .
.....See (528, 5).	40. Make the solution with the following proportions: 1 gram of $\text{Am}_2\text{MoO}_4$ is dissolved in 12.5 cc. of strong $\text{AmHO}$ which has been previously mixed with an equal quantity of water; the solution is allowed to stand, if necessary, till clear, then poured off into 25 cc. of strong $\text{HNO}_3$ ; the liquid will become hot, and should be allowed to stand until it is cool before being used.
.....In powder.	
.....In small pieces.	
.....In small crystals.	
.....Solid in pieces.	
.....1 : 12 [40 grams].	
.....1 : 12 [40 grams].	
In pieces as large as a pea.	

40 a. The  $\text{HNO}_3$  solution of this salt must yield no precipitate with  $\text{AgNO}_3$ .41. Must leave no residue on evaporation; in separate portions no precipitates must be caused by  $\text{BaCl}_2$ ,  $\text{AgNO}_3$  or  $\text{Am}_2\text{C}_2\text{O}_4$ , neither must any precipitate or even dark coloration be produced by addition of  $\text{Am}_2\text{S}$ .42. The proportion by weight should be 1 : 10 of water; it is best kept in green glass bottles, as it slowly dissolves  $\text{Pb}$  from white flint glass. The solution must not become dark in color when mixed with  $\text{H}_2\text{S}$ , nor give a gelatinous precipitate ( $\text{Al}_2\text{HO}_6$ ) when mixed with excess of  $\text{AmCl}$  solution.43. Dry finely powdered  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  are intimately mixed in the proportion of 53 : 69 by weight, and kept in a stoppered bottle.44. Pure powdered  $\text{BaCO}_3$  is either purchased, or is made by precipitating  $\text{BaCl}_2$  solution completely with  $\text{Am}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  solution, and washing the precipitate well by decantation. This powder is then mixed with distilled water to the consistency of thin cream.45. Dissolve 20 grams of  $\text{NaA}$  in 60 cc. of distilled water, and add to the solution 40 cc. of strong  $\text{HA}$ .46. By neutralizing strong hot  $\text{Na}_2\text{CO}_3$  solution with  $\text{HNO}_3$  and evaporating to dryness. Sold also as Chili saltpetre.

47. Purchased and kept in gutta-percha bottles.

reagents entered apart.

## PREPARATION OF SATURATED SOLUTIONS.

By a "saturated solution" is meant a solution containing the maximum quantity of the substance which the solvent can dissolve; this quantity varies with the temperature of the solution; the solutions spoken of in this book are saturated at the ordinary temperature.

## PREPARATION OF SATURATED SOLUTIONS OF SOLIDS.

**527.** The method described in (515) may be used, or the substance in powder may be constantly shaken up with the solvent for some time, and the solution then separated from excess of the solid by decantation or filtration. The most ready method of preparing a saturated solution of  $\text{Ca}(\text{HO})_2$ , or of  $\text{CaSO}_4$ , is to pour some of the powder into a Winchester quart, then fill it up to the shoulder with water, and mix the powder thoroughly with the water by shaking the bottle; the shaking is repeated at intervals during half an hour or more; the bottle is then allowed to stand until the excess of powder has settled and the liquid above it is quite clear, when the liquid is poured off into another "Winchester," leaving the powder behind; fresh water is poured upon this powder and more solution made as above by constant shaking, the bottle being allowed to stand by until the fresh supply is required. By thus making a fresh stock of solution whenever one lot is decanted, time is allowed for the freshly prepared solution to become perfectly clear before it is required for use.

1. *Lime-water* is made in the above manner by shaking slaked lime in powder with common *tap-water*.

2. *Calcium sulphate* solution is prepared by saturating *distilled water* by the above means with gypsum or plaster of Paris in powder.

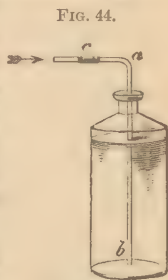
## PREPARATION OF SATURATED SOLUTIONS OF GASES.

**528.** The gas is made to bubble in a constant stream from the end of a glass tube which dips nearly to the bottom of the liquid (Fig. 44); the liquid must be kept cold, and be contained in a bottle which is fitted with an accurately ground stopper. In order to ascertain whether the solution is saturated, the bubbles of the gas are occasionally watched to see whether they diminish in size as they rise through the liquid; if they do not, the bottle, after being closed tightly by the thumb or by inserting the stopper, is violently shaken; if this causes a pressure and escape of gas from the bottle into the air on unclosing its mouth, the liquid is saturated; if, on the contrary, it causes a pressure of air into the bottle, the gas must be passed again for some time, and the trial repeated, until on shaking, as directed above, an outward pressure is noticed.

*Note.*—All the preparations mentioned below should be made in a draught cupboard, as the gases are injurious to the lungs if inhaled.

1. *Sulphuretted hydrogen solution* is made by fitting the bent tube *a b* (Fig. 44), by means of the india-rubber joint *c*, upon either of the apparatus described in (500) for the preparation of  $H_2S$ ; the gas is thus made to bubble through the distilled water (best recently boiled to expel air, and cooled) until it is saturated. The solution should not be made in large quantities at a time, as it gradually decomposes, depositing sulphur and losing its smell; it is then unfit for use.

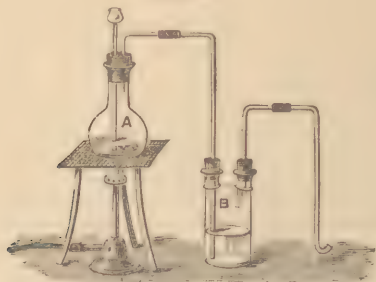
2. *Sulphurous acid solution* is prepared by passing sulphur dioxide gas into distilled water until it is saturated. The gas is made by heating scraps of copper with strong  $H_2SO_4$  in a glass flask fitted as is shown in A (Fig. 45). The gas passes from the flask through some water contained in a washing-bottle as shown at B (Fig. 45), and from this bottle into the distilled water (Fig. 44) through the tube *a b*, which is connected with the outlet tube of the washing-bottle





by means of the india-rubber joint *c*. The solution must be kept in a well-stoppered bottle.

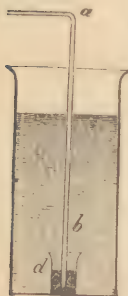
FIG. 45.



3. *Chlorine-water*.—Chlorine gas is made in the apparatus shown in Fig. 45, by gently heating manganic oxide in lumps or powder in the flask A with some strong commercial hydrochloric acid, previously mixed with a third of its volume of water. The gas bubbles through a little water in the washing-bottle B, and thence through the bent tube *a b* into the distilled water (Fig. 44). This solution must be kept in a dark place, or in a bottle which is coated with black paper, as it undergoes alteration by light.

4. *Hydrofluosilicic acid* is made by passing silicon fluoride gas into water. The gas is prepared in a flask

FIG. 46.

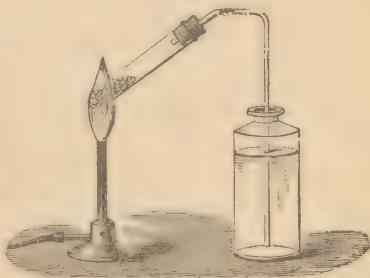


fitted as shown in A, Fig. 45. Into this flask there is first poured an intimate mixture of 50 grams of dry, pure, finely powdered fluor-spar with 50 grams of fine white sand; 300 grams of strong  $\text{H}_2\text{SO}_4$  are then poured into the flask through the funnel-tube, and the acid is mixed with the powder by shaking it round in the flask; the gas is caused to be evolved by gently heating the flask, and is made to pass first through the bottle B (Fig. 45), which must be empty and dry inside; thence it escapes through a bent tube *a b* (Fig. 46), which is fitted upon the outlet tube of B by an india-rubber joint; the end of

the tube, *a b*, is made to dip into mercury contained in a small beaker *d* (Fig. 46), which stands in a large beaker containing 400 cc. of water. As soon as the silicon fluoride gas comes into the water, after escaping from the mercury, it is decomposed into hydrofluosilicic acid, which dissolves in the water, and silica, which remains suspended in the water as a gelatinous mass; the silica very soon closes the end of the delivery-tube *a b* unless it is kept immersed in the mercury. As the current of gas slackens, the heat is raised, until white fumes of  $\text{H}_2\text{SO}_4$  begin to appear in the preparation-flask; the process is then arrested and the gelatinous silica is separated from the solution by squeezing the latter through fine muslin and afterwards filtering it if not quite clear. The silica may be dried, heated strongly in a porcelain dish, and put by in a stoppered bottle as reagent No. 86 (526), for which it serves admirably.

5. *Nitrogen-tetroxide Solution*.—Lead nitrate in dry pieces is heated in a test-tube fitted with cork and delivery-tube (Fig. 47), and the red fumes which escape are passed into dilute  $\text{H}_2\text{SO}_4$ . Care must be taken to maintain the heat uniformly after the fumes begin to be evolved, else the liquid may be sucked back into the hot tube by the contraction of the gas on cooling; also the delivery-tube must be removed from the liquid as soon as the heating is stopped.

FIG. 47.



## 529. SOLUTIONS FOR THE

*Note.*—Each bottle should bear on its label the number, name, and formula the solutions, containing the powdered solid of each of those substances on their label the name, number, and formula of the substance.

1. Reference number.	2. Name.  [The numbers in brackets refer to similarly numbered remarks in the last column.]	3. Formula.
100.s.	Potassium chloride.....	KCl
101.s.	Ammonium chloride.....	AmCl
102.s.	Sodium chloride.....	NaCl
103.s.	Magnesium sulphate.....	MgSO <sub>4</sub> .7H <sub>2</sub> O
104.	Barium chloride.....	Bar. 10. 2H <sub>2</sub> O
105.	Strontium nitrate.....	Sr(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O
106.	Calcium chloride.....	CaCl <sub>2</sub> .6H <sub>2</sub> O
107.s.	{ Alum, or Aluminium potassium sulphate } .....	AlK(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O
108.s.	Ferric chloride (a) <sup>1</sup> .....	Fe <sub>2</sub> Cl <sub>3</sub>
109.s.	Ferrous sulphate (a) <sup>2</sup> .....	FeSO <sub>4</sub> .7H <sub>2</sub> O
110.s.	{ Chrome alum, or Chromium potassium sulphate } .....	CrK(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O
111.s.	Zinc sulphate.....	ZnSO <sub>4</sub> .7H <sub>2</sub> O
112.s.	Manganese chloride (a).....	MnCl <sub>2</sub>
113.s.	Nickel sulphate.....	NiSO <sub>4</sub> .7H <sub>2</sub> O
114.s.	Cobalt nitrate.....	Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O
115.s.	Mercuric chloride.....	HgCl <sub>2</sub>
116.s.	Lead acetate (a) <sup>2</sup> .....	PbAc <sub>2</sub> .3H <sub>2</sub> O
117.s.	Bismuth nitrate (a) <sup>2</sup> .....	Bi(NO <sub>3</sub> ) <sub>3</sub> .5H <sub>2</sub> O
118.s.	Copper sulphate (a).....	CuSO <sub>4</sub> .6H <sub>2</sub> O
119.s.	Cadmium sulphate (a).....	CdSO <sub>4</sub> .4H <sub>2</sub> O
120.s.	{ Arsenious oxide (a) (a) <sup>1</sup> Solution in dilute HCl } .....	As <sub>2</sub> O <sub>3</sub>
120.	{ Arsenious oxide (a) (a) <sup>2</sup> Solution in water.....	
121.s.	Sodium arsenate.....	Na <sub>2</sub> HAsO <sub>4</sub> .12H <sub>2</sub> O
122.s.	Antimonious chloride (a) <sup>2</sup> .....	SbCl <sub>3</sub>
123.s.	Stannous chloride (a) <sup>2</sup> .....	SnCl <sub>2</sub> .2H <sub>2</sub> O
124.	Stannic chloride (a) <sup>2</sup> .....	SnCl <sub>4</sub>
125.	Silver nitrate.....	AgNO <sub>3</sub>
126.	Mercurous nitrate (a) <sup>2</sup> .....	Hg <sub>2</sub> NO <sub>3</sub> .2H <sub>2</sub> O

<sup>1</sup> a signifies that the solid substance is not

<sup>2</sup> Solid Sb<sub>2</sub>O<sub>3</sub> or K(SbO)T (Tartar emetic)

## REACTIONS OF THE METALS.

of the substance. Small 4-ounce wide-mouthed bottles should be kept near whose number has a small (s) affixed to it; these bottles should also carry

4. Weight of solid in grams to be dissolved in one "Winchester."	5. Proportion by weight of solid to water.	6. Remarks.
		[These numbers correspond to the small reference numbers in brackets in the second column.]
100	1 : 25	48. The solution must be made acid with a little $H_2SO_4$ , and some clean iron nails kept in it, or better, a small quantity is freshly prepared when required (p. 329, 34, col. 5).
200	1 : 12	
50	1 : 50	49. A little HA must be added to this solution to make it clear.
50	1 : 50	
25	1 : 100	50. 25 grams of $Bi(NO_3)_3$ must be dissolved by heating with 25 cc. of strong HCl diluted with 25 of water; this solution is cooled and poured into the bottle, and the measure made up by pouring in dilute HCl containing one-twentieth of its volume of strong HCl.
100	1 : 25	
100 (in crystals)	1 : 12	51. Dissolve 10 grams of $As_2O_3$ by heating it with 50 cc. of strong HCl mixed with 50 cc. of water, and dilute to the Winchester quart.
200	1 : 12	
25	1 : 100	52. Boil excess of $As_2O_3$ for several minutes with 200 cc. of water, filter and dilute to the quart. <sup>3</sup>
25	1 : 100	
50	1 : 50	53. 28 grains of crystallized $SbCl_3$ are dissolved in 25 cc. of strong HCl mixed with 25 cc. of water, and diluted to the quart <sup>3</sup> with HCl mixed with four times its measure of water.
25	1 : 100	
25	1 : 100	54. Boil 25 grams of $SnCl_2$ with 50 cc. of strong HCl mixed with 50 cc. of water; as soon as it has dissolved to a clear solution dilute to the quart. <sup>3</sup> Scraps of Sn must be kept in the bottle.
50	1 : 50	
25	1 : 100	55. Heat 25 grams of $SnCl_2$ with 25 cc. of strong HCl and 100 cc. of water; whilst constantly stirring, add $KClO_3$ to the hot solution until the liquid turns yellow and Cl is smelt, boil off the Cl and dilute to the quart. <sup>3</sup>
25	1 : 100	
25	1 : 100	56. Dissolve by warming 25 grams of $Hg_2(NO_3)_2$ with 6 cc. of strong $HNO_3$ diluted with 114 cc. of water, then pour water into this solution until it is diluted to a quart. <sup>3</sup> Keep Hg in the bottom of the bottle.
25	1 : 100	

in the crystalline condition.

may be used for the blowpipe reaction.

<sup>3</sup> Winchester quart.

## 530. SOLUTIONS FOR THE

*Note.*—Refer to note at the head of the preceding table (529), which is pared amongst the reagents (524, 525, 526), and the solutions for reactions

1. Reference Number.	2. Name. [The small numbers in brackets refer to the corresponding numbers in the sixth column.]	3. Formula.
130	Sodium sulphate.....	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
131.s.	{ Sodium carbonate <sup>(33)</sup> .....	$\text{Na}_2\text{CO}_3$
	{ Marble (calcium carbonate) <sup>(33)</sup> .....	$\text{CaCO}_3$
132.s.	{ Ferrous sulphide <sup>(38)</sup> .....	$\text{FeS}$
	{ Ammonium sulphide <sup>(38)</sup> .....	$\text{Am}_2\text{S}$
133.s.	Acid sodium sulphite.....	$\text{NaHSO}_3$
134.	Sodium hyposulphite.....	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
135.	Sodium hypochlorite <sup>(39)</sup> .....	$\text{Na}_2\text{Cl}_2\text{O}$
136.s.	Potassium nitrite (a).....	$\text{KNO}_2$
137.s.	Potassium nitrate.....	$\text{KNO}_3$
138.s.	Potassium chlorate.....	$\text{KClO}_3$
139.s.	Sodium chloride <sup>(40)</sup> .....	$\text{NaCl}$
140.s.	Sodium bromide.....	$\text{NaBr}$
141.s.	Potassium iodide.....	$\text{KI}$
142.	Sodium phosphate.....	$\text{Na}_3\text{HPO}_4 \cdot 12\text{H}_2\text{O}$
143.	Sodium arsenate <sup>(41)</sup> .....	$\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$
144.s.	Borax <sup>(42)</sup> .....	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
145.	Potassium bichromate.....	$\text{K}_2\text{Cr}_2\text{O}_7$
146.s.	{ Sodium silicate <sup>(43)</sup> .....	$\text{Na}_2\text{SiO}_3$
	{ Silica (white sand).....	$\text{SiO}_2$
147.s.	Fluor-spar (calcium fluoride).....	$\text{CaF}_2$
148.	Hydrofluosilicic acid <sup>(44)</sup> .....	$\text{H}_2\text{SiF}_6$
149.s.	Potassium cyanide <sup>(45)</sup> .....	$\text{KCy}$
150.	Potassium ferrocyanide.....	$\text{K}_4\text{FeCy}_6 \cdot 3\text{H}_2\text{O}$
151.	Potassium ferricyanide.....	$\text{K}_3\text{Fe}_2\text{Cy}_{12}$
152.	Potassium sulphocyanide.....	$\text{KCyS}$
153.s.	Ammonium oxalate <sup>(46)</sup> .....	$\text{Am}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
154.s.	{ Tartaric acid <sup>(47)</sup> .....	$\text{H}_2\text{T}$
	{ Sodium tartrate <sup>(48)</sup> .....	$\text{Na}_2\text{T} \cdot 2\text{H}_2\text{O}$
155.s.	Sodium acetate <sup>(49)</sup> .....	$\text{NaA} \cdot 3\text{H}_2\text{O}$



## REACTIONS OF THE ACID-RADICLES.

also applicable to this. Many of the solutions in this list are already pre-  
for metals (529).

4.	5.	6.
Weight of solid in grams to be dissolved in one Winchester quart	Proportion by weight of solid to water.	Remarks. [The numbers correspond to the small reference numbers in brackets in the second column.]
25	1 : 100	57. The $\text{Na}_2\text{CO}_3$ is required only in the solid form, and can be taken from the reagent bottle on the working bench, No. 18 (524). The marble is kept in small pieces as large as a pea; it is found in reagent bottle No. 79 (526).
100	1 : 25	58. The $\text{FeS}$ is kept as a solid in small pieces as large as a pea. The $\text{Am}_2\text{S}$ can be taken from reagent bottle No. 7, on the working bench.
100	1 : 25	
100	1 : 25	59. Strong "Liquor Sodæ Chlorinatæ," diluted with an equal measure of water.
100	1 : 25	
50	1 : 50	60. No. 102, paragraph 529.
50	1 : 50	61. No. 121, paragraph 529.
50	1 : 50	62. No. 19, paragraph 524.
12	1 : 200	63. The solution is made by dissolving 100 grams of the thick syrup, sold as "soluble glass," in water, and diluting to the Winchester quart. The solid substance to be used is sand finely ground.
50	1 : 50	
50	1 : 50	64. No. 35, paragraph 525.
25	1 : 100	65. No. 42, paragraph 525. The solution decom- poses by keeping; a little solid is dissolved when required.
25	1 : 100	
25	1 : 100	66. No. 9, paragraph 524.
100	1 : 25	67. No. 30, paragraph 525.
	1 : 10	68. 123 grams of $\text{H}_3\text{T}$ are dissolved by heat in 500 cc. of water, the hot solution is exactly neu- tralized with solid $\text{Na}_2\text{CO}_3$ , and then diluted to a Winchester quart.
In fine powder.		69. A little of the solid substance (see No. 41, 525) is dissolved, when required, in water.

## 531. CHEMICALS REQUIRED FOR SECTION I.

In the following list those substances which are used for Section I only are marked by letters of the alphabet. The bottles containing these substances should be arranged apart in alphabetical order. Against others a number is placed; this indicates that the substance is used for analytical purposes, and will therefore be found, together with any necessary descriptive remarks, in one of the foregoing lists (524, 525, 526, 529, 530).

*Note.*—All numbers below 22 refer to bottles standing on the shelves above the working bench. If a substance is required for more than one experiment, its entry is not repeated.

Letter or number of reference.	Name.	Formula.	Remarks.
A.	Mercuric oxide, . . .	HgO.	The orange-colored <i>precipitated</i> oxide is best.
20.	Potassium chlorate, . .	KClO <sub>3</sub> .	
B.	Manganese dioxide, . .	MnO <sub>2</sub> .	Commercial oxide in powder.
C.	Wood-charcoal, . . .	C.	In pieces as large as a hazelnut.
57.	Lime-water, . . .	Ca(HO) <sub>2</sub> .	
D.	Sulphur, . . .	S.	Pieces of roll sulphur as large as a pea.
21.	{ Litmus and turmeric } { papers, . . . } { . . . }	—	—
59.	Potassium dichromate, .	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .	
E.	Phosphorus, . . .	P.	Pieces as large as half a pea, kept in a stoppered bottle under water.
F.	Granulated zinc, . . .	Zn.	Not necessarily pure.
G.	Hydrochloric acid, . . .	HCl.	Strong, commercial.
H.	Marble, . . .	CaCO <sub>3</sub> .	In pieces not larger than a hazelnut.
I.	Copper, . . .	Cu.	Turnings, clippings, or filings.
J.	Nitric acid, . . .	HNO <sub>3</sub> .	Strong, commercial.
K.	Ammonium chloride, . .	NH <sub>4</sub> Cl.	Solid, commercial.
32.	Slaked lime, . . .	Ca(HO) <sub>2</sub> .	
L.	Oxalic acid, . . .	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> 2H <sub>2</sub> O.	Solid, in crystals.
M.	Sulphuric acid, . . .	H <sub>2</sub> SO <sub>4</sub> .	Strong, commercial.
N.	Sodium hydrate, . . .	NaHO.	Strong solution in water.
O.	"Turkey red," . . .	—	In strips.
P.	Sodium chloride, . . .	NaCl.	In pieces as large as a hazelnut broken from a lump of rock-salt.
3.	Nitric acid, . . .	HNO <sub>3</sub> .	
48.	Silver nitrate, . . .	AgNO <sub>3</sub> .	
6.	Ammonium hydrate, . .	NH <sub>4</sub> HO.	
9.	Ammonium oxalate, . .	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	
17.	Barium chloride, . . .	BaCl <sub>2</sub> .	
7.	Ammonium sulphide, . .	(NH <sub>4</sub> ) <sub>2</sub> S.	
39.	Potassium nitrate, . .	KNO <sub>3</sub> .	

### 532. CHEMICALS REQUIRED FOR THE EXPERIMENTS ON ANALYTICAL OPERATIONS (SECTION III).

All the substances, with those exceptions<sup>1</sup> only which are named in this list, are required either for analytical purposes (see lists in paragraphs 524, 525, 526, 529, 530), where they may be found by the number placed in the first column; or they are already entered on the list of substances required for experiments on the gases (531), where they may be found by the reference letter in the first column. A letter (s) affixed to the number of reference indicates that the substance is required in the solid condition; see note at heading of (529).

Number or letter of reference.	Name.	Formula.
39.	Potassium nitrate.....	$\text{KNO}_3$
118.s.	Copper sulphate.....	$\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$
79.	Marble.....	$\text{CaCO}_3$
2.	Hydrochloric acid.....	$\text{HCl}$
45.	Copper.....	$\text{Cu}$
3.	Nitric acid.....	$\text{HNO}_3$
17.	Barium chloride.....	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
8.	Ammonium carbonate.....	$\text{Am}_2\text{CO}_3$
161. <sup>1</sup>	Filter-paper.....	In sheet, or cut.
1.	Sulphuric acid.....	$\text{H}_2\text{SO}_4$
A.	Mercuric oxide.....	$\text{HgO}$
K.	Ammonium chloride.....	$\text{NH}_4\text{Cl}$
100.s.	Potassium chloride.....	$\text{KCl}$
18.	Sodium carbonate.....	$\text{Na}_2\text{CO}_3$
112.s.	Manganese chloride.....	$\text{MnCl}_2$
19	Borax.....	$\text{Na}_2\text{B}_4\text{O}_7$
62.s.	Ferrous sulphate.....	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
102.	Sodium chloride.....	$\text{NaCl}$
160. <sup>1</sup>	Wool-charcoal.....	$\text{C}$
116.s.	Lead acetate.....	$\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$
—	Red cabbage leaves.....	—
6.	Ammonium hydrate.....	$\text{NH}_4\text{HO}$
5.	Ammonium chloride.....	$\text{NH}_4\text{Cl}$
21.	(Litmus-paper.....	—
	(Turmeric-paper.....	—

<sup>1</sup> The exceptions are Nos. 160 and 161, which numbers refer to paragraph 533; also the red cabbage leaves, which are readily obtainable.

**533. SUNDRY OTHER REQUISITES NOT INCLUDED IN THE PRECEDING LISTS.**

Reference number.	Name and description.
160.	<i>Wood-charcoal</i> .—This may be purchased in small pieces commonly used for fuel. If required for blowpipe experiments (33), the charcoal should be tolerably free from cracks and from bark. It may be sawn into convenient shape and size by a fine-toothed saw.
161.	<i>Filter-paper</i> may be bought in sheets which are cut into squares of the required size; these are folded and cut as directed in experiment 40 (p. 61). Ready cut circular filters can also be purchased, which only require to be folded.
162.	<i>Corks</i> .—These should be obtained as free as possible from holes or cracks; they must be sound and easily softened by pressure. All sizes between $1\frac{1}{2}$ inch and $\frac{1}{2}$ inch in diameter should be kept in stock. For wash-bottles and other permanently fitted apparatus in which the cork is not subjected to much heating, the india-rubber stoppers are much to be preferred to corks, since they are almost imperishable and retain their elasticity very much longer than corks do.

# SUBSTANCES TO BE GIVEN FOR ANALYSIS BY THE PRECEDING TABLES AND DIRECTIONS.

**534.** It must be understood that the substances mentioned below are merely brought forward as examples of what may be given to the student for analysis; the teacher will use his own judgment in adopting and extending the list.

**535. SUBSTANCES FOR ANALYSIS WHILST TRYING THOUGH THE REACTIONS FOR METALS AND ACID-RADICLES.**

If the student, after working through the reactions for each of the metallic groups, intends to analyze substances containing one member only, or any two or more members, of that group, it is a good plan to analyze first a few substances containing only one member and to gradually increase the number present in those subsequently given. It is well to keep these substances in the dissolved state<sup>1</sup> as a rule, as they are intended mainly to afford practice in separation and detection according to the group tables, and the time spent by the student in preparing the solution is therefore wasted. Occasionally, however, a solid substance may be given in which the metal or acid-radicle present is to be detected by blow-pipe tests or other tests made on the solid substance.

As examples of the substances to be given, in the order best suited to the gradual advance in difficulty, the following, selected for Groups V, IV, and III B, will serve:

<i>Group V.</i>	<i>Group IV.</i>	<i>Group III b.</i>
Solution of NaCl	Solution of BaCl <sub>2</sub> .2H <sub>2</sub> O	Solution of ZnSO <sub>4</sub> .7H <sub>2</sub> O
" " NH <sub>4</sub> Cl	" " Sr(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O	" " MnCl <sub>2</sub>
" " KCl	" " CaCl <sub>2</sub> .6H <sub>2</sub> O	" " NiSO <sub>4</sub> .7H <sub>2</sub> O
" " NaCl + KCl	" " Sr(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O	" " Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O
" " NaCl + NH <sub>4</sub> Cl + KCl	" " BaCl <sub>2</sub> .2H <sub>2</sub> O + Sr(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O	" " MnCl <sub>2</sub> + ZnSO <sub>4</sub> .7H <sub>2</sub> O
" " NaCl + NH <sub>4</sub> Cl	" " BaCl <sub>2</sub> .2H <sub>2</sub> O + Sr(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O	" " Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O + NiSO <sub>4</sub> .7H <sub>2</sub> O + ZnSO <sub>4</sub> .7H <sub>2</sub> O
" " MgSO <sub>4</sub> .7H <sub>2</sub> O + NaCl + KCl	" " BaCl <sub>2</sub> .2H <sub>2</sub> O + Sr(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O	etc., etc., etc.
<i>Solids:</i> NaCl, NH <sub>4</sub> Cl, KCl, AmCl + NaCl, etc.		<i>Solids:</i> MnCl <sub>2</sub> , NiSO <sub>4</sub> .7H <sub>2</sub> O, Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O, ZnSO <sub>4</sub> .7H <sub>2</sub> O, etc.

<sup>1</sup> The solutions already made for the reactions (529, 530) will serve very well for this purpose, being given either singly or mixed.



536. Substances are given to be tested for the members of an acid-radicle group in the same order (535),<sup>1</sup> the first substances containing one member only, those subsequently given containing two or more members of the group.

537. SUBSTANCES FOR ANALYSIS BY THE DIRECTIONS CONTAINED IN SECTION V.

Any one of the solutions named in paragraphs 529 and 530 may be given for analysis by Section V, some of them being neutral, some acid, and others alkaline in reaction. The following more difficult solutions with acid or alkaline reaction may also be added to the list :

<i>Acid.</i>	<i>Alkaline.</i>
$\text{Ca}_3(\text{PO}_4)_2$ , "Bone-ash" dissolved in dilute HCl.	$\text{KSbO}_3$ dissolved in water.
$\text{BaCO}_3$ dissolved in dilute HCl.	$\text{Na}_2\text{SiO}_3$ , solution of "soluble glass."
$\text{Mg}(\text{BO}_2)_2$ " " HCl.	$\text{Na}_2\text{SnO}_3$ , "preparing salt" of the dyer.
$\text{BaCrO}_4$ " " HCl.	

Any of the solid salts which were dissolved in order to prepare the solutions in paragraphs 529 and 530, may be given for analysis as solid substances by (331 *et seq.*).

As examples of substances possessing metallic appearance (366), the following may be mentioned as suitable for analysis :

Zn, in pieces or filings.	NiAs, Kupfernickel.
Pb " "	Graphite, or Black lead.
$\text{FeS}_2$ , Iron Pyrites.	Iron filings.

As insoluble substances which require to be examined by (367 *et seq.*), the following may be given for analysis :

$\text{BaSO}_4$ .	$\text{CaF}_2$ , Fluor spar.
$\text{PbSO}_4$ .	$\text{FeCr}_2\text{O}_4$ , Chrome Iron Ore.
AgCl.	S, as pieces of roll sulphur.
$\text{SnO}_2$ , Tinstone.	C, as powdered wood-charcoal or plumbago.

<sup>1</sup> See footnote on page 341.

<sup>2</sup> Made by mixing hot solutions of  $\text{Na}_2\text{B}_4\text{O}_7$  and  $\text{Mg}(\text{NO}_3)_2$ .

### 538. SOLID SUBSTANCES TO BE ANALYZED BY THE PRELIMINARY EXAMINATIONS.

For the Preliminary Examination for Metals (387):

<i>Simple.</i>			<i>Complex.</i>	
NH <sub>4</sub> Cl HgCl <sub>2</sub> As <sub>2</sub> O <sub>3</sub> KNO <sub>3</sub> Cr <sub>2</sub> O <sub>3</sub>	Pb(NO <sub>3</sub> ) <sub>2</sub> NaCl BaCl <sub>2</sub> .2H <sub>2</sub> O Sr(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O CuSO <sub>4</sub> .6H <sub>2</sub> O (See note.)	ZnSO <sub>4</sub> .7H <sub>2</sub> O MnCl <sub>2</sub> Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O NiSO <sub>4</sub> .7H <sub>2</sub> O SnO <sub>2</sub>	AmCl + NaCl HgCl <sub>2</sub> + BaCl <sub>2</sub> .2H <sub>2</sub> O MnCl <sub>2</sub> + KCl NiSO <sub>4</sub> .7H <sub>2</sub> O + ZnSO <sub>4</sub> .7H <sub>2</sub> O	AlK(SO <sub>4</sub> ) <sub>3</sub> .12H <sub>2</sub> O SnO <sub>2</sub> + Sr(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O CaCO <sub>3</sub> + ZnSO <sub>4</sub> .7H <sub>2</sub> O Cr <sub>2</sub> O <sub>3</sub> + MnCl <sub>2</sub> + NaCl

*Note.*—Best finely powdered, since its color is then almost destroyed.

For the Preliminary Examination for Acid-radicles (410):

<i>Simple.</i>			<i>Complex.</i>
CaCO <sub>3</sub> Na <sub>2</sub> SO <sub>3</sub> .7H <sub>2</sub> O CaCl <sub>2</sub> O NaCl	FeS KNO <sub>3</sub> KClO <sub>3</sub> KI	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .5H <sub>2</sub> O KBr NaA	CaCO <sub>3</sub> + KNO <sub>3</sub> CaCl <sub>2</sub> O + CaF <sub>2</sub> Na <sub>2</sub> CO <sub>3</sub> + KI

A few of the above-mentioned solids may then be examined by both preliminary examinations for both metals and acid-radicles.

### 539. SUBSTANCES TO BE ANALYZED BY THE GENERAL COURSE (380 *et seq.*).

The following lists are so arranged that the analysis of the substances contained in them is more difficult in each column proceeding from left to right, and usually also in proceeding in one and the same column from top to bottom. For examples of alkaline solutions, see (537):

## SUBSTANCES FOR ANALYSIS BY THE GENERAL COURSE.

1. Simple soluble substances.	2. Complex soluble substances.	3. Complex soluble substances.
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ $\text{MnCl}_2$ $\text{HgCl}_2$ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ $\text{KCl}$ $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ $^1\text{CaCO}_3$ $\text{Pb}(\text{NO}_3)_2$ $^1\text{As}_2\text{O}_3$ $\text{Fe}_2\text{Cl}_6$ $\text{NH}_4\text{Cl}$ $\text{NaCl}$ etc., etc.	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \text{BaCl}_2 \cdot 2\text{H}_2\text{O} + \text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} + \text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ $\text{MnCl}_2 + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ $\text{Pb}(\text{NO}_3)_2 + \text{HgCl}_2 + \text{NaCl}$ $^1\text{As}_2\text{O}_3 + \text{CaCO}_3 + \text{BaCO}_3$ $^2\text{ZnO} + \text{MgCO}_3 + \text{KClO}_3$ $^1\text{MgCO}_3 + \text{BaCO}_3 + \text{PbCO}_3$ etc., etc.	$\left\{ \begin{array}{l} \text{Fe}_2\text{Cl}_6 \\ \text{MnCl}_2 \\ \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \\ \text{KCl} \end{array} \right.$ $\left\{ \begin{array}{l} \text{As}_2\text{O}_3 \\ \text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \\ \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \end{array} \right.$ $\left\{ \begin{array}{l} \text{Hg}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O} \\ \text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \\ \text{KNO}_3 \\ \text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O} \\ \text{etc., etc.} \end{array} \right.$

4. Substances yielding a phosphate precipitate in Group III.	5. Substances partly or entirely insoluble.	
$\left\{ \begin{array}{l} \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \\ \text{Fe}_2\text{Cl}_6 \\ \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \end{array} \right.$ $\left\{ \begin{array}{l} \text{BaCl}_2 \cdot 2\text{H}_2\text{O} \\ \text{MgCl}_2 \\ \text{Fe}_2\text{Cl}_6 \\ \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \end{array} \right.$ $\left\{ \begin{array}{l} \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \\ \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \\ \text{MnCl}_2 \\ \text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \\ \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \\ \text{etc., etc.} \end{array} \right.$	$\text{BaSO}_4$ $\text{SiO}_2 + \text{S}$ $\text{BaSO}_4 + \text{CaF}_2 + \text{SnO}_2$ $\left\{ \begin{array}{l} \text{BaCl}_2 \cdot 2\text{H}_2\text{O} \\ \text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \\ \text{AgNO}_3 \end{array} \right.$ $\left\{ \begin{array}{l} \text{SiO}_2 \\ \text{S} \\ \text{C} \end{array} \right.$ $\text{PbSO}_4 + \text{BaSO}_4$ $\text{PbCrO}_4$ , ignited.	<i>Metallic substances (467 et seq.).</i> Iron pyrites ( $\text{FeS}_2$ ) Iron filings ( $\text{Fe}$ ) Zinc clippings ( $\text{Zn}$ ) Brass filings ( $\text{Cu} + \text{Zn}$ ) German silver ( $\text{Cu} + \text{Zn} + \text{Ni}$ ) Bronze ( $\text{Cu} + \text{Sn}$ ) Type metal ( $\text{Sb} + \text{Sn} + \text{Pb}$ )  <i>Silicates (480).</i> Fire-clay ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) Brown clay (do. + $\text{Fe}$ ) Window glass ( $\text{Na}, \text{Ca}, \text{SiO}_2$ ) Flint glass ( $\text{Pb}, \text{K}, \text{SiO}_2$ )  <i>Cyanogen Compounds (482).</i> Any of the foregoing which has been mixed with $\text{KCyan}$ , $\text{K}_4\text{FeCy}_6 \cdot 3\text{H}_2\text{O}$ , $\text{K}_3\text{Fe}_2\text{Cy}_{12}$ , $\text{K}_6\text{Co}_2\text{Cy}_{12}$

<sup>1</sup> To be given in the solid state.

## APPENDIX I.

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### REACTIONS FOR THE RARER ELEMENTS.

THIS Appendix contains some of the most important reactions for many of the rarer elements. The arrangement here used is that adopted in Section IV, those elements being placed together which are precipitated in the same analytical group; the groups, however, are arranged in the order in which they occur in the general table. A scheme for the detection of these elements follows (553), showing in which group they are precipitated in the general table, and by which reactions they will be most readily found.

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#### GROUP I.—SILVER GROUP.

In this group are included Tl and Wo; the former is partially precipitated as chloride by HCl, the latter completely as tungstic acid.

Thallium is only partially precipitated in Group I since its chloride is not quite insoluble in water; it belongs also to Group III B, being entirely precipitated by  $\text{Am}_2\text{S}$ .

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#### 540. THALLIUM (Tl).—Use $\text{Tl}_2\text{SO}_4$ solution.

Tl occurs in small quantity in many natural sulphides, often also in the ashes of plants and in mineral waters. Tl yields both *thallie* and *thallious* salts, but the former are very unstable, changing even when their solutions are heated into *thallious* salts.

*HCl*: a white precipitate which rapidly settles, does not blacken in the light, and is soluble in aqua regia. It is soluble in a large quantity of water, and therefore does not form in dilute solutions.

*KI*: a yellow precipitate; almost insoluble in water, more soluble in *KI* solution. In a solution containing *Fe*, any ferric salt must first be reduced by  $\text{H}_2\text{SO}_3$  before adding *KI*.

*PtCl*<sub>4</sub>: orange-red precipitate, slightly soluble in water.

*Am*<sub>2</sub>*S*: black precipitate, which is easily coagulated by heat, is insoluble in *AmHO*, alkaline sulphides, and in *KCy*; it is readily oxidized by the air to  $\text{Ti}_2\text{SO}_4$ , and is easily soluble in mineral acids. *Tl* is entirely precipitated by  $\text{H}_2\text{S}$  from a solution in which *HAc* is the only free acid present, but free mineral acids prevent the precipitation entirely.

*Flame Coloration*.—Thallium compounds impart to the Bunsen flame an intense *green* color, which, however, rapidly disappears. The spectrum (p. 361) is very characteristic, consisting of one bright emerald-green line. Thallium may be easily detected by the spectroscope in solution, or better in any of its precipitates mentioned above.

#### 541. TUNGSTATES.—Use $\text{Na}_2\text{WO}_4$ solution.

*W* usually occurs in the form of a tungstate. The insoluble tungstates yield soluble alkaline tungstates on being fused with alkaline carbonates. From a solution of alkaline tungstate *HCl* precipitates the tungstic acid entirely.

*HCl*, *HNO*<sub>3</sub>, or  $\text{H}_2\text{SO}_4$ : white precipitate ( $\text{H}_2\text{WO}_4$ ), becoming yellow on boiling; insoluble in excess of acid, but soluble in *AmHO*. A piece of *Zn* dropped into the acid liquid containing the precipitate yields a deep-blue color.

*SnCl*<sub>2</sub> in neutral solution, made by dissolving  $\text{SnCl}_2$  crystals in water and filtering: *yellow* precipitate becoming *blue* on addition of *HCl* and heating.

*Am*<sub>2</sub>*S* yields no precipitate in a solution of alkaline tungstate; but if, after adding *Am*<sub>2</sub>*S*, the liquid is made acid with *HCl*, brown *WS*<sub>3</sub> is precipitated.

*Microcosmic bead*:

In outer flame—*Colorless* or *yellow*.

In inner flame—*Blue*: if a little  $\text{FeSO}_4$  is fused into the bead the color changes to *blood-red*. These colors are best seen when the bead is perfectly cold.

#### GROUP II A.—COPPER GROUP.

In this group are included *Pd* (*Os*, *Rh*, *Ru*); they are precipitated as sulphides by  $\text{H}_2\text{S}$  from acid solutions, and the sulphides are insoluble in *Am*<sub>2</sub>*S*, and in caustic alkali solution.



**542. PALLADIUM (Pd).—Use  $\text{PdCl}_2$  solution.**

Pd occurs as a metal in native platinum, also in gold and silver. Palladium solutions are reddish-brown, or yellow if dilute; addition of water precipitates a basic salt, unless sufficient free acid is present to prevent it.

$\text{H}_2\text{S}$ : black precipitate, in neutral, alkaline, and acid solutions; insoluble in  $\text{Am}_2\text{S}$ , but soluble in boiling  $\text{HCl}$  or in aqua regia.

$\text{AmHIO}$ : flesh-colored precipitate ( $\text{PdCl}_2 \cdot 2\text{NH}_3$ ); soluble in excess of  $\text{AmHIO}$  to a colorless liquid, from which  $\text{HCl}$  precipitates yellow crystalline paladammonium-chloride ( $\text{N}_2\text{H}_6\text{Pd}^{++}\text{Cl}_2$ ).

$\text{HgCy}_2$ : yellowish-white gelatinous precipitate ( $\text{PdCy}_2$ ), slightly soluble in  $\text{HCl}$ , easily soluble in  $\text{AmHIO}$ . Very characteristic reaction.

$\text{KI}$ : black precipitate ( $\text{PdI}_2$ ). Very characteristic.

**GROUP II B.—ARSENIC GROUP.**

In this group are included Mo, Se, Te (Ir).

**543. MOLYBDATES (Mo).—Use  $\text{Am}_2\text{MoO}_4$  solution.**

Mo occurs as molybdate; also as sulphide which may be readily converted into  $\text{MoO}_3$  by ignition in the air or by heating with  $\text{HNO}_3$ . Unignited  $\text{MoO}_3$  dissolves in acids; ignited  $\text{MoO}_3$  is insoluble in acids, but easily soluble in alkalis.

$\text{HCl}$ ,  $\text{HNO}_3$ , or  $\text{H}_2\text{SO}_4$  added in small quantity to an aqueous solution of a molybdate, yields a precipitate which is readily soluble in excess of the acid.

$\text{H}_2\text{S}$  added in *very small* quantity to the acidified solution, gives a *blue* liquid, in larger quantities a *brown* precipitate ( $\text{MoS}_3$ ); the precipitation becomes complete only when the solution is heated and  $\text{H}_2\text{S}$  passed for some time; the precipitate is soluble in solutions of alkaline sulphides and hydrates, from which it is reprecipitated by acid added in excess.

$\text{Zn}$  or  $\text{SnCl}_2$ , added to a solution of a molybdate in  $\text{HCl}$ , colors it *brown*, *green*, or *blue*, according to its state of concentration.

$\text{KCyS}$ , added to a solution acidified with  $\text{HCl}$ , gives no coloration; but on dropping in a piece of  $\text{Zn}$  a beautiful *crimson* color is produced, which, when the liquid is shaken with ether, is taken up by the ether.

$\text{Na}_2\text{HPO}_4$ , added in very small quantity to a solution of a molybdate, acidified with  $\text{HNO}_3$ , gives, on gently warming the liquid, a yellow precipitate readily soluble in excess of alkali-hydrate solution.

*Borax bead*: outer flame, *yellow*; inner, *dark brown*.

*Microcosmic bead*: outer and inner flames, *green*.

**544. SELENIUM (Se).—**Use a metallic selenide, an alkaline selenite and selenate.

Se occurs as metallic selenides, *e. g.*, of Fe, Cu, Ag. A selenide heated in an open tube evolves a smell of decaying horseradish, and produces a gray or red sublimate of Se; the smell is very characteristic.

*a. Selenites :*

$H_2S$  gives in acid solutions, if cold a *yellow*, if hot a *red-dish-yellow*, precipitate; soluble in  $Am_2S$ ,

$BaCl_2$  in neutral solutions a white precipitate; soluble in  $HCl$  or  $HNO_3$ .

$SnCl_2$  or  $H_2SO_3$  gives in the presence of free  $HCl$  a red, or in warm solutions a gray precipitate of Se.

$Cu$  in a hot  $HCl$  solution becomes covered with a black film; the liquid on standing with the  $Cu$  for some time becomes colored red with Se.

*b. Selenates :*

$HCl$  produces no change in the cold; but on boiling,  $Cl$  is given off and the selenate is reduced to selenite, to which the above tests under (*a*) may be applied.

$BaCl_2$ : a white precipitate ( $BaSeO_4$ ); insoluble in cold  $HCl$ , dissolved by boiling with  $HCl$  with evolution of  $Cl$  and reduction to  $BaSeO_3$ .

*c. Selenium in any form of combination* is detected by the following reactions:

Heated on charcoal in the inner blowpipe flame a smell of rotten horseradish is perceived.

Fused on charcoal with  $Na_2CO_3$  in the inner blowpipe flame, a fused mass is obtained, which when moistened on  $Ag$  yields a black stain, and on addition of  $HCl$  evolves  $H_2Se$ , a badly smelling gas.

**545. TELLURIUM (Te).—**Use a metallic telluride, an alkaline tellurite and tellurate.

Te occurs united with metals, *e. g.*, Au, Ag, Bi, Cu, Pb.

A telluride heated in an open glass tube gives white fumes and a sublimate which differs from that given by  $Sb$ , by being fusible before the blowpipe.

*a. Tellurites :*

$H_2O$ : on dilution with water tellurous acid is precipitated from the acid solution.

$H_2S$ : in acid solutions a brown precipitate ( $TeS_2$ ); easily soluble in  $Am_2S$ .

$H_2SO_3$ ,  $SnCl_2$  or  $Zn$  precipitates black Te.

- b. *Tellurates*.—HCl produces no change in the cold; but on boiling, Cl is evolved and the tellurate is reduced tellurite; the solution then gives the above reactions under (a).
- c. *Tellurium in any form of combination*, if fused with  $\text{Na}_2\text{CO}_3$  on charcoal in the inner blowpipe flame, gives sodium telluride; a solution of which gives a black stain on Ag, and on being acidified deposits black Te and evolves  $\text{H}_2\text{Te}$ .

### GROUP III.—IRON AND ZINC GROUPS.

In this Group are included U, In, Ti, Be, Tl [V], (Zr, Ce, Ta, Nb, La, Di, Y, E, Th).

Tl is often partially precipitated as chloride in Group I, and its reactions are given under that group. V is not precipitated by  $\text{Am}_2\text{S}$  unless acid is added in excess after  $\text{Am}_2\text{S}$ .

#### 546. URANIUM (U).—Use $(\text{UO}_2)''(\text{NO}_3)_2$ .

U occurs in nature principally as *pitchblende* (oxide), also as *uranite* (a hydrated uranium-calcium phosphate) and *chalcolite* (hydrated uranium-copper phosphate).

$\text{AmHIO}$ ,  $\text{KHIO}$ , or  $\text{NaHIO}$ : yellow precipitate insoluble in excess.

$\text{Am}_2\text{S}$  gives in neutral solutions a *dingy-yellow* or *brown* precipitate of uranium oxysulphide, which is soluble in  $\text{Am}_2\text{CO}_3$  (diff. from  $\text{ZnS}$ ,  $\text{MnS}$ ,  $\text{FeS}$ , etc.). The precipitate settles slowly unless  $\text{AmCl}$  is added; it is soluble in acids, even in  $\text{HA}$ ; on being heated with  $\text{Am}_2\text{S}$  in excess it is changed into uranious oxide and sulphur.

$\text{H}_2\text{S}$  produces no precipitate in acid solutions.

$\text{Am}_2\text{CO}_3$ ,  $\text{KHCO}_3$ , or  $\text{NaHCO}_3$ : yellow precipitate easily soluble in excess; from this solution the uranium is reprecipitated by addition of  $\text{NaHIO}$  or  $\text{KHIO}$ , or by boiling (diff. from Fe).

$\text{K}_4\text{FeC}_6$  gives in acid solutions a reddish-brown precipitate, which is distinguished from the similar one produced in a copper solution by dissolving in excess of  $\text{AmHIO}$  to a *yellow* fluid.

$\text{BaCO}_3$ : complete precipitation even in the cold.

Zn changes the *yellow* color of acid solutions to *green*.

*Borax and Microcosmic beads:*

Outer flame *yellow*; inner flame, *green*.

#### 547. INDIUM (In).

*Alkali-hydrates* precipitate a hydrate resembling  $\text{Al}_2\text{HO}_6$ , insoluble in excess. Indium solutions are also precipitated by

alkaline carbonates, by  $\text{Na}_2\text{HPO}_4$ , by boiling their neutral solution with  $\text{NaA}$ , by  $\text{BaCO}_3$ , and by alkaline oxalates.

$\text{H}_2\text{S}$  gives no precipitate in strong acid solutions; in dilute and feebly acid solutions a little sulphide separates; in a solution containing no free acid but  $\text{HA}$  the metal is entirely precipitated as *yellow* sulphide; the precipitate is insoluble in cold, soluble in boiling  $\text{Am}_2\text{S}$ ; from the boiling solution *white* sulphide separates on cooling.

$\text{Am}_2\text{S}$ , added after  $\text{H}_2\text{T}$  and excess of  $\text{AmHIO}$ , gives a *white* precipitate, becoming *yellow* on treatment with  $\text{HA}$ .

*Flame coloration*: bluish-violet. The spectrum shows two very characteristic blue lines, which are brilliant, but very rapidly disappear when the chloride is employed; see p. 361.

**548. BERYLLIUM (Be).**—Occurs as silicate in phenakite, and as silicate with Al-silicate in beryl and emerald.

$\text{Am}_2\text{S}$ ,  $\text{AmHIO}$ ,  $\text{KHIO}$ , or  $\text{NaHIO}$ : flocculent hydrate is precipitated resembling  $\text{Al}_2\text{HIO}_6$  in its appearance, and in being soluble in  $\text{KHIO}$ . Differs from  $\text{Al}_2\text{HIO}_6$  in being precipitated from its solution in  $\text{KHIO}$  by dilution and long boiling, and by being soluble when freshly precipitated if it is long boiled with  $\text{AmCl}$  solution.

*Alkaline carbonates* precipitate a carbonate soluble in excess, especially in  $\text{Am}_2\text{CO}_3$ ; from these solutions the carbonate is reprecipitated, on diluting and boiling for some time, with especial ease from the  $\text{Am}_2\text{CO}_3$  solution (diff. from Al).

$\text{BaCO}_3$  precipitates Be solutions completely;  $\text{H}_2\text{C}_2\text{O}_4$  and alkaline oxalates produce no precipitate. Moistened with  $\text{Co}(\text{NO}_3)_2$  solution and heated on charcoal in the outer blowpipe flame, a *gray* mass is obtained (diff. from Al).

**549. TITANIUM (Ti).**—Occurs as  $\text{TiO}_2$ , with traces of Fe, Mn, Cr, in rutile, anatase, and brookite; also as  $\text{TiO}_2$  in combination with Fe in titaniferous iron ore.

Ignited  $\text{TiO}_2$  is insoluble in water and most acids; it is easily soluble in  $\text{HF}$ , less readily in boiling strong  $\text{H}_2\text{SO}_4$ ; it is also rendered soluble in cold water by fusion with  $\text{KHSO}_4$ .

$\text{TiO}_2$  differs from  $\text{SiO}_2$  in not being volatilized when heated in a platinum dish with  $\text{HF}$  and strong  $\text{H}_2\text{SO}_4$ .

By dilution and long boiling, white flocculent hydrated  $\text{TiO}_2$  is precipitated from solutions in  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ , and from the aqueous solution of the fusion with  $\text{KHSO}_4$ ; the precipitate is metatitanic acid; it cannot be filtered off unless an acid or  $\text{AmCl}$  is added.

$\text{AmHfO}$ ,  $\text{KHfO}$ ,  $\text{NaHfO}$ ,  $\text{Am}_2\text{S}$ , or  $\text{BaCO}_3$ , white flocculent precipitate insoluble in excess; if precipitated and washed in the cold it dissolves in  $\text{HCl}$  and in dilute  $\text{H}_2\text{SO}_4$ .

$\text{Zn}$  or  $\text{Sn}$  gives in acid solutions a *blue*, or if dilute a *rose-colored*, liquid.

$\text{Na}_2\text{S}_2\text{O}_3$ , on boiling, precipitates  $\text{Ti}$  solution entirely (diff. from  $\text{Fe}$ ).

*Microcosmic bead:*

In the outer flame; *yellow*, whilst hot; *colorless*, cold.

In the inner flame; *yellow*, hot; *violet*, cold. The production of these colors is much aided by adding a fragment of  $\text{Sn}$ . Addition of a small quantity of  $\text{FeSO}_4$  gives in the inner flame a *blood-red* bead.

## 550. VANADIUM (V).

Occurs in vanadinite [ $3\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbCl}_2$ ], and in certain  $\text{Fe}$  and  $\text{Cu}$  ores.

Vanadium is known in several stages of oxidation; it will usually occur in analysis as vanadic acid or a vanadate, which in acid solution is of a yellow or reddish color.

$\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_3$ , or  $\text{H}_2\text{C}_2\text{O}_4$  reduces acid solutions of a vanadate, and causes the color of the solution to change to *blue*; with  $\text{H}_2\text{S}$  a deposit of sulphur also forms.

$\text{Am}_2\text{S}$ , if added in excess, gives a brown liquid, in which an excess of acid causes a *brown* precipitate of  $\text{V}_2\text{S}_5$ ; excess of  $\text{Am}_2\text{S}$  dissolves this to a reddish-brown liquid.

$\text{Zn}$  gives in a very dilute solution, acidified with  $\text{H}_2\text{SO}_4$  and gently warmed, a *blue* color, which changes into *green* and then *lavender-blue*.

Solid  $\text{AmCl}$ , added until the solution is saturated, precipitates  $\text{Am}_3\text{VO}_4$ , which is insoluble in saturated  $\text{AmCl}$  solution. Very characteristic reaction.

$\text{H}_2\text{O}_2$  when shaken up with an acid solution imparts a red color, which is not removed by shaking with ether. This is a very delicate test.

*Borax bead:*

In outer flame: *colorless*, or *yellow* if much  $\text{V}$  is present.

In inner flame: *green*, hot and cold; if much  $\text{V}$  is present *brown* hot, and *green* cold.



## GROUP V.—POTASSIUM GROUP.

In this group are included Li, Cs, Rb.

## 551. LITHIUM (Li).

Li occurs frequently in mineral waters and in the ashes of plants; also in small quantities in the minerals lepidolite, triphane, and petallite. It is allied to the Barium Group by the difficult solubility of its carbonate and phosphate; and it differs from K and  $\text{NH}_4$  by not being precipitated by  $\text{PtCl}_4$  or by  $\text{H}_2\text{T}$ ; from Na it is readily distinguished by the flame coloration and spectroscopic.  $\text{LiCl}$  is separated from  $\text{KCl}$  and  $\text{NaCl}$  by its insolubility in a mixture of absolute alcohol and ether.

$\text{Na}_2\text{HPO}_4$  added to the not too dilute solution, made decidedly alkaline with  $\text{NaHO}$ , gives, on boiling, a white crystalline precipitate ( $\text{Li}_3\text{PO}_4$ ) which quickly settles. Traces of Li may be precipitated by adding  $\text{Na}_2\text{HPO}_4$ , then  $\text{NaHO}$  until the liquid remains alkaline, evaporating to dryness and washing the residue with dilute  $\text{AmHO}$ . This precipitate differs from the phosphates of Ba, Sr, Ca, and Mg by fusing in the blowpipe flame and being absorbed by the charcoal support, also by its diluted solution in  $\text{HCl}$  giving no precipitate on addition of  $\text{AmHO}$  in excess in the cold, but a white crystalline precipitate on boiling.

*Flame coloration*: this is *carmine-red*; the spectrum (see p. 361) consists of two lines, an intense carmine-red line ( $\alpha$ ) and a feeble orange-yellow line ( $\beta$ ). This coloration is concealed by that of Na, which, however, does not interfere with the spectrum: the Na coloration is also removed if the flame is viewed through the indigo-prism, whereas that of Li can pass through the thinner parts of the prism; it differs from the K coloration, however, in being unable to penetrate to thick layers of indigo solution or in being much weakened by its passage. As silicate, Li only gives the flame coloration after fusion with  $\text{CaSO}_4$ ; the phosphate requires to be first moistened with  $\text{HCl}$ .

## 552. RUBIDIUM (Rb), and CÆSIUM (Cs).

These metals occur in small quantities in some mineral waters and in a few minerals. Their compounds resemble those of K in being precipitated by  $\text{PtCl}_4$  and by  $\text{H}_2\text{T}$ , and in giving a similar flame coloration. Characteristic differences are, the much greater insolubility in water of the platino-chlorides, which enables the  $\text{K}_2\text{PtCl}_6$  to be dissolved away from  $\text{Rb}_2\text{PtCl}_6$  and  $\text{Cs}_2\text{PtCl}_6$  by boiling the precipitate with success-

sive small quantities of water; the alums also show a similar difference in solubility in cold water.

Cs and Rb are readily distinguished from one another and from other elements by their spectra (see p. 361). For Cs the blue lines ( $\alpha, \beta$ ) are especially distinct and characteristic; in the Rb spectrum the indigo-blue lines ( $\alpha, \beta$ ) are very distinct, but the red lines ( $\gamma, \delta$ ) are most characteristic. For the spectroscopic test the chlorides are most suitable.

## 553. GENERAL GROUP TABLE FOR

## Group I.—Reagent HCl.

The group pp. may contain in addition to  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{PbCl}_2$ :

$\text{TiCl}$  (white).  
 $\text{H}_2\text{WO}_4$  ( " ).

$\text{TiCl}$  will usually be readily detected by a spectroscopic examination of the group pp. It may be removed from the group pp. by boiling with a little water, and ppd. from the cold filtrate by  $\text{KI}$  ( $\text{Pb}$  is also thus ppd.): the pp. is yellow, and gives the thallium spectrum.

$\text{H}_2\text{WO}_4$ : a white pp. becoming yellow on boiling. Its presence is confirmed by dropping a piece of  $\text{Zn}$  into a portion of the acid liquid and pp., when a deep-blue color will be obtained.

Also by fusion of the pp. in a microcosmic bead, which will be colorless or yellow in the outer flame, blue (or with  $\text{FeSO}_4$ , blood-red) in the inner flame.

Group II.—Reagent  $\text{H}_2\text{S}$ .

The group pp. may contain as sulphides, in addition to  $\text{Hg}$ ,  $\text{Pb}$ ,  $\text{Bi}$ ,  $\text{Cu}$ ,  $\text{Cd}$ :

$\text{Pd}$  (black-brown)  
 $\text{Ti}$  (black; ppd. with  $\text{As}_2\text{S}_3$ )  
 $[\text{Os}, \text{Rh}, \text{Ru}]^1$  } Insoluble in  $\text{Am}_2\text{S}$ .

And in addition to  $\text{SnS}$ ,  $\text{SnS}_2$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{As}_2\text{S}_3$ ,  
 $\text{Au}_2\text{S}_3$ ,  $\text{PtS}_2$ :

$[\text{Ir-sulphide}]^1$   
 $\text{Mo-}$  " (brown)  
 $\text{Se-}$  " (red-yellow)  
 $\text{Te-}$  " (black) } Soluble in  $\text{Am}_2\text{S}$ .

The yellow color of a solution containing  $\text{V}$  is changed to blue by  $\text{H}_2\text{S}$ .

$\text{Ti}$  is readily found by the spectroscope in the group pp.

$\text{Pd}$  will remain in solution in excess of  $\text{AmHO}$  with  $\text{Cd}$  and  $\text{Cu}$  in Table II A: from this solution it is ppd. by adding  $\text{HCl}$ : its presence may be further confirmed by the  $\text{HgCy}_2$  or  $\text{KI}$  tests (542).

The examination of the sulphides in Group II B when the above elements may be present is best commenced by fusion with  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$ . From the fused mass, water dissolves sodium-arsenate, -molybdate, -selenate, and -tellurate, leaving  $\text{SnO}_2$ , sodium-antimonate,  $\text{Au}$ ,  $\text{Pt}$ , and  $\text{Ir}$  undissolved; the elements may then be detected by special tests. For the separation and detection of the platinum metals a larger work must be consulted.

<sup>1</sup> Only completely ppd. if the liquid has been warmed, and  $\text{H}_2\text{S}$  passed for a long time.

## PRECIPITATION OF RARER ELEMENTS.

Group III.—Reagents $\text{AmCl}$ , $\text{AmHO}$ , and $\text{Am}_2\text{S}$ .	Precipitated from the filtrate from Group III by excess of $\text{HCl}$ .	Group V.
The group pp. may contain as sulphides, in addition to $\text{Fe}$ , $\text{Zn}$ , $\text{Mn}$ , $\text{Ni}$ , $\text{Co}$ :	As sulphides: $V$ (black). $W$ (trace, brown). $Ni$ (trace, black).	The filtrate after the separation of all the group precipitates may contain besides $\text{Mg}$ , $\text{K}$ , and $\text{Na}$ :
$U$ (black-brown). $In$ ( " ). $Tl$ ( " ).		$Li$ , $Cs$ , $Rb$ .
And as hydrates in addition to $Al$ , $Cr$ (and phosphates, etc.):	This pp. is dried and then fused with a mixture of $\text{Na}_2\text{CO}_3$ and $\text{KNO}_3$ ; on boiling the mass with water, $\text{NiO}$ remains undissolved; it is filtered off, and its presence confirmed by fusion in a borax bead.	These metals are readily detected by their very characteristic spectra (p. 361). $\text{LiCl}$ may also be detected by its behavior with $\text{Na}_2\text{HPO}_4$ .
$Ti$ (white, flocculent). $Be$ (colorless, gelatinous). $Zr$ " " " $Ta$ , $Nb$ , $Ce$ , $La$ , $Di$ , $Y$ , $E$ , $Th$ .]	The aqueous solution may contain alkaline vanadate and tungstate. $V$ is separated by saturating the liquid with $\text{AmCl}$ , and its presence confirmed in the pp. by the borax bead, and by dissolving the pp. in $\text{HCl}$ and employing the reactions with $\text{H}_2\text{O}_2$ and with $\text{Zn}$ (550).	Before proceeding to the spectroscopic examination, it is well to convert them into chlorides if they are not already in that form.
$Tl$ and $In$ will usually be readily detected by a spectroscopic examination of the pp.	The filtrate, after concentration if necessary, is acidified with $\text{HCl}$ , and the presence of $W$ confirmed by the $\text{Zn}$ reaction and the microcosmic bead (541).	If the chlorides are evaporated to dryness and extracted with absolute ether and alcohol, to which a few drops of $\text{HCl}$ have been added, $\text{LiCl}$ , $\text{RbCl}$ , $\text{CsCl}$ dissolve, whilst the greater part of the $\text{KCl}$ and $\text{NaCl}$ remains undissolved.
$Tl$ may be first separated and detected by dissolving some of the group pp. in boiling dilute $\text{HCl}$ , and reducing any $\text{Fe}$ present in the solution by $\text{H}_2\text{SO}_5$ ; then precipitating $Tl$ by addition of $\text{KI}$ , and testing the pp. by the spectroscope.		The solution is evaporated to dryness, dissolved in a little $\text{HCl}$ , and $\text{Rb}$ and $\text{Cs}$ are ppd. by $\text{PtCl}_4$ ; this pp. is boiled with small quantities of water until it no longer gives the $\text{K}$ spectrum; the spectra of $\text{Rb}$ and $\text{Cs}$ will then be seen, if present. $Li$ is found in the filtrate after adding $\text{PtCl}_4$ .
A more complete scheme for the analysis of this group pp. will be found in par. 554 (pp. 356, 357).		

## 554. TABLE FOR ANALYSIS OF GROUP III PRECIPITATE,

The precipitate may contain Fe, U, In, Tl, Al, Cr, Zn,

After a preliminary spectroscopic examination has been made of a small portion of the the general table (553), the group pp. is dried and fused in platinum with  $\text{KHSO}_4$  for long time with cold water:

<i>Residue</i> may contain $\text{Ta}_2\text{O}_5$ , $\text{Nb}_2\text{O}_5$ , also $\text{SiO}_2$ , and traces of Fe and Cr which have escaped solution. By fusion with $\text{KClO}_3$ and $\text{NaHO}$ , Cr and Si are rendered soluble in dilute $\text{NaHO}$ ; from the residue, insoluble in $\text{NaHO}$ , $\text{Ta}_2\text{O}_5$ and $\text{Nb}_2\text{O}_5$ may be removed by washing with dilute $\text{Na}_2\text{CO}_3$ solution.	<i>Solution</i> : reduce Fe by adding $\text{H}_2\text{SO}_4$ in excess, dilute considering the vessel, and by passing a stream of $\text{CO}_2$ through it,
	<i>Pp.</i> may consist of $\text{TiO}_2$ ; possibly also traces of Zr.
	Confirm the presence of $\text{TiO}_2$ by the micro-cosmic bead (549).
	<i>Filtrate</i> : add a few drops of strong $\text{HNO}_3$ , and precipitate once more by adding excess
	<i>Pp.</i> may contain Fe, In, U, Cr, Al, Be, etc.
	<i>Pp.</i> may contain Fe, In, U, etc. Dissolve large excess of $\text{HCl}$ , add $\text{BaCO}_3$ , and let
	<i>Pp.</i> may contain Fe, In, U, also traces of Al and Cr.
	It is dissolved in $\text{HCl}$ , and $\text{NaHCO}_3$ is added in excess, whereby U alone is obtained in solution.
	In is found by the spectroscope.
	Cr by fusion with $\text{Na}_2\text{CO}_3$ and $\text{KClO}_3$ .
	<i>Filtrate</i> may contain Th, Ba is pptd. by $\text{H}_2\text{SO}_4$ , the liquid exactly neutralized or $\text{K}_2\text{SO}_4$ are added, allowed to stand for pp. is washed with
	<i>Pp.</i> may contain Zr, Th, Ce.
	Th and Ce are dissolved away by boiling with dilute $\text{HCl}$ , and are reppd. by $\text{AmHO}$ .



## WHEN THE RARER ELEMENTS MAY BE PRESENT (FRESSENIUS).

Mn, Ni, Co, Ti, Be, [Zr, Ta, Nb, Ce, La, Di, Y, E, Th].

pp. for Ti and In, and Ti has been further tested for, if necessary, by KI as directed in some time, the cold mass is then powdered and allowed to stand, with shaking, for a

ably and boil for a long time, preserving the liquid from oxidation by the air by unless it smells constantly of  $\text{SO}_2$ :

concentrate by evaporation, and add  $\text{AmHO}$  in excess; filter, dissolve the pp. in  $\text{HCl}$ , of  $\text{AmHO}$ :

Dissolve it in  $\text{HCl}$ , and add excess of cold strong  $\text{KHO}$  solution:

in  $\text{HCl}$ , boil off any stand:

Zr, Ce, La, Di, V, E, adding excess of is concentrated and with  $\text{KHO}$ . Crystals and the liquid is some hours. The  $\text{K}_2\text{SO}_4$  solution.

*Filtrate* may contain Al, Cr, Be; dilute and boil for some time, filter. Al remains in solution, and may be ppd. by adding  $\text{HCl}$  just in excess, then  $\text{AmHO}$  in excess.

Cr and Be are separated by fusion with  $\text{Na}_2\text{CO}_3$  and  $\text{KClO}_3$ , dissolving in water and ppd.; Be by adding  $\text{HNO}_3$  in excess, then  $\text{AmHO}$  in excess.

*Filtrate* may contain:

Zn, Mn, Ni, Co.

*Soln.* may contain Y, E, also Be.

The solution is ppd. by  $\text{AmHO}$ , and Be dissolved away from it by  $\text{H}_2\text{C}_2\text{O}_4$ .

## APPENDIX II.

### USE OF THE SPECTROSCOPE FOR ANALYSIS.

555. When the light from a bright gas or candle flame is allowed to pass through a narrow slit, and is then looked at through an appropriately cut-glass prism, a series of colors is seen following one another without break or interruption; such a band of colors has received the name of a "continuous spectrum." The direct-vision spectroscope<sup>1</sup> is a little instrument furnished at one end with the requisite slit, whose width may be varied by means of a projecting screw-collar; at the other end will be found a draw-tube containing lenses for focussing, and the body of the instrument incloses the glass prisms. On looking at a bright gas or candle flame through this spectroscope a "continuous spectrum" will be seen, whose margins may be sharply focussed by means of the draw-tube. A similar spectrum is seen when any brightly glowing *non-volatile* substance is viewed through the spectroscope.

Many substances, however, when strongly heated, volatilize; and their *glowing vapors* emit light whose color is in many cases peculiar and characteristic; mention has been already made of this fact in par. 32, and its importance as a means of detecting certain elements was there stated.

When such a vapor is viewed through the spectroscope, a "discontinuous" or "line spectrum" is seen, which consists of one or more colored "lines" or "bands," whose position and color are characteristic of that particular vapor. Thus Na vapor yields one bright-yellow line, Li one intense carmine line, whilst K gives two lines, one red and the other violet. These lines are readily seen by holding in the Bunsen flame a loop of platinum wire, which has been previously dipped into strong NaCl, LiCl, or KCl solution, and viewing the colored flame through the spectroscope. But not only does this method of analysis serve to detect the elements when occurring separately, it also detects each of them when two or more are present together, since the spectrum of each is then seen without any interference from the others; thus although the *flame coloration* of K or of

<sup>1</sup> This is the cheapest and most handy form of spectroscope, and may be purchased of the makers, Messrs. Browning, of the Strand, London.

Li is entirely masked by that of Na when the chlorides of both metals are held in the flame together, the two *spectra* are distinctly seen side by side when the flame is looked at through the spectroscope; and both Li and K are thus readily recognized when present with Na.

The delicacy of this method of detection is extreme; thus the  $\frac{1}{1000000}$ th of a gram of Na can be distinguished by the appearance of its yellow spectral line.

The accompanying chart (p. 361) gives the relative position of the most important lines in eleven different spectra. It is meant to serve merely as a guide to the beginner; when the student has accustomed himself to the appearance of the spectra, reference to the chart will become unnecessary.

It is important to remember that the coloration of the Bunsen flame can only be produced by substances which are volatile at the temperature of the flame; and that the coloration due to any element is more intense the more volatile is the compound employed. Thus KCl and KNO<sub>3</sub> are readily volatilized in the flame, and color it strongly; K<sub>2</sub>SO<sub>4</sub> is somewhat less volatile, and the coloration it yields is correspondingly feeble; K<sub>2</sub>CO<sub>3</sub> is still less volatile, and imparts little color to the flame; whilst K<sub>2</sub>SiO<sub>3</sub> is non-volatile, and yields no flame coloration whatever. Hence in testing for an element by the spectroscope, care must be taken to insure its conversion, if present, into a form of combination which is volatile in the Bunsen flame. As a rule, chlorides and nitrates of the metals are the most volatile salts, sulphates are less volatile, carbonates still less so, and silicates are usually non-volatile. It is in many cases sufficient to moisten the substance upon the platinum wire loop with strong H<sub>2</sub>SO<sub>4</sub> or HCl before introducing it into the flame; the sulphates of Ba, Sr, and Ca should be first reduced to sulphides by heating them in the inner blow-pipe flame; the sulphides are then readily converted into chlorides by moistening them with HCl. K<sub>2</sub>SiO<sub>3</sub> in a natural silicate yields no K flame coloration; by fusion of the powdered mineral with gypsum powder, however, the K<sub>2</sub>SiO<sub>3</sub> is converted into K<sub>2</sub>SO<sub>4</sub>, and the sulphate yields the K coloration readily:



Owing to the invariable presence of small quantities of Na in atmospheric dust, and to the extreme delicacy of the spectroscopic reaction for Na, the Bunsen flame always shows the Na line when looked at through the spectroscope, and the brightness of the line may be increased by striking the table, or in any other way raising dust, in the neighborhood of the flame. This is in several respects advantageous; since, by rendering the Na line distinct by regulating the width of the slit and the position of the focussing lens, the spectroscope may be placed in adjustment before introducing into the flame the substance whose spectrum is to be observed. The Na line further serves as a fixed point from which the position of the lines of other elements may be judged; and in order to assist the student in so using it, the position of the Na line is indicated in all the other spectra on the accompanying chart by means of a dotted line.

**556.** When working with the spectroscope, the Bunsen flame should be so placed as to have a dark background, in order that light from

*the flame only* may enter the slit; if not working in a darkened room, a piece of black velvet or cloth may be hung behind the flame; this is, however, not indispensable; it will usually be sufficient to avoid the entrance of direct or brightly reflected light into the instrument. It is best to view first either the sky, or a bright flame—such as that obtained by closing the air-holes at the foot of the Bunsen burner, and to turn the spectroscope into such a position that the continuous spectrum becomes horizontal with its red end to the left hand; the instrument is next directed on a portion of the non-luminous Bunsen flame about two-thirds of the height from the flame's base, and held either by a clamp, or very steadily by the hand, in this position. The Na line is then focussed as directed above; and, whilst carefully watching the flame through the spectroscope, the substance is introduced into the outer part of the front of the flame at about one-third the flame's height from its base; the observation of the flame is continued for a short time after moistening the substance with acid as directed above. The careful observation of the flame during the introduction of the substance into the flame is necessary, since some elements (*e. g.*, Th, when present in small quantity, give a spectrum which appears only as a momentary flash; other substances appear only as the substance attains the full temperature of the flame, and their spectra are therefore seen only after the substance has been heated in the flame for some time.

The regulation of the width of the slit must depend upon circumstances. A wide slit admits more light and increases the brightness of the lines; a narrow slit causes the lines to be more widely separated, and thus prevents neighboring lines from blending, and generally enables their position to be more accurately noted. It is well to use a narrow slit, unless working with a faint flame coloration, or unless lines of feeble intensity have to be looked for.

The spectroscope is more especially useful in qualitative analysis:

1st. In detecting readily K and Li, and other substances whose flame colorations are masked by that of Na, when occurring with Na.

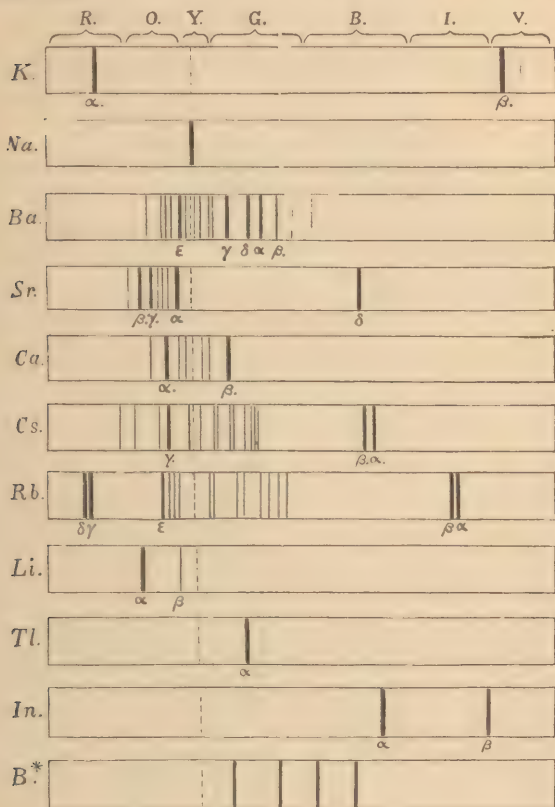
2d. It also rapidly distinguishes Sr from Ca; since as shown in the chart the Sr spectrum contains a characteristic blue line  $\delta$ , as well as certain red lines situated to the left hand of all those in the Ca spectrum; the green line  $\beta$  of Ca is also very distinctive of that element. Ba is specially characterized by the four green lines,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ .

3d. The spectroscope is of great value for detecting the rarer metals Li, In, Th, Cs, Rb, which usually occur in comparatively small quantity in nature; the last four of these metals were first searched after and discovered on account of their very marked spectra having been seen by the spectroscope.

**557. Spectrum Chart.**—In using the chart below, the color of a line in any spectrum may be found by referring to the head of the chart, and seeing in which of the bracketed spaces it falls; above each bracket is placed the initial letter of the name of the color; the colors run from left to right in the following order: Red, Orange, Yellow, Green, Blue, Indigo, Violet.

The chart is a reduction from Bunsen's map: the relative position of the lines is given correctly; those in each spectrum which are most striking or characteristic are made thicker than the rest, and

are denoted by Greek letters in the order of their relative importance. Many of the thin lines will not be seen by means of a small pocket spectroscope.



\* This spectrum is seen when boric acid or a borate is fused with a little  $\text{Na}_2\text{CO}_3$  on a loop of platinum wire, and the flame coloration obtained from this bead is examined.



## APPENDIX III

### 558. LIST OF CHEMICAL ELEMENTS, WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

*Note.*—The words in brackets are the Latin names of the elements from which the symbols have been derived.

Name.	Symbol	Atomic Weight.	Name.	Symbol	Atomic Weight.
Aluminium.....	Al	27.5	Molybdenum.....	Mo	96
Antimony (stibium).....	Sb	122	Nickel.....	Ni	59
Arsenicum.....	As	75	Niobium.....	Nb	94
Barium.....	Ba	137	Nitrogen.....	N	14
Bismuth.....	Bi	210	Osmium.....	Os	199
Boron.....	B	11	Oxygen.....	O	16
Bromine.....	Br	80	Palladium.....	Pd	106
Cadmium.....	Cd	112	Phosphorus.....	P	31
Cæsium.....	Cs	133	Platinum.....	Pt	197
Calcium.....	Ca	40	Potassium (kalium).....	K	39
Carbon.....	C	12	Rhodium.....	Rh	104
Cerium.....	Ce	92	Rubidium.....	Rb	85
Chlorine.....	Cl	35.5	Ruthenium.....	Ru	104
Chromium.....	Cr	52.5	Selenium.....	Se	79.5
Cobalt.....	Co	59	Silicon.....	Si	28
Copper (cuprum).....	Cu	63.5	Silver (argentum).....	Ag	108
Didymium.....	D	96	Sodium (natrium).....	Na	23
Erbium.....	E	112	Strontium.....	Sr	87.5
Fluorine.....	F	19	Sulphur.....	S	32
Glucium.....	G	9.5	Tantalum.....	Ta	182
Gold (aurum).....	Au	197	Tellurium.....	Te	129
Hydrogen.....	H	1	Thallium.....	Tl	204
Indium.....	In	113.4	Thorium.....	Th	238
Iodine.....	I	127	Tin (stannum).....	Sn	118
Iridium.....	Ir	197	Titanium.....	Ti	50
Iron (ferrum).....	Fe	56	Tungsten (wolframium).....	W	184
Lanthanum.....	La	92	Uranium.....	U	120
Lead (plumbum).....	Pb	207	Vanadium.....	V	51
Lithium.....	L	7	Yttrium.....	Y	62
Magnesium.....	Mg	24	Zinc.....	Zn	65
Manganese.....	Mn	55	Zirconium.....	Zr	89
Mercury (hydrargyrum).....	Hg	200			

### 559. THERMOMETRIC SCALES.

There are two different thermometric scales in use in this country, the Centigrade and Fahrenheit; the former of these is rapidly becoming universal for scientific purposes. The two scales are mutually

convertible by the following formulæ, in which  $F.^{\circ}$  represents a temperature on the Fahrenheit scale,  $C.^{\circ}$  a temperature on the Centigrade scale:

$$\left. \begin{array}{l} (F.^{\circ} - 32) = C.^{\circ} \\ C.^{\circ} + 32 = F.^{\circ} \end{array} \right\} \text{degrees}$$

The temperatures occasionally referred to in this treatise are given on the Centigrade scale.

## WEIGHTS AND MEASURES.

**560.** The corresponding values of the French and English weights and measures are here given; the use of the French or decimal system is strongly recommended by its extreme simplicity, since the smaller denominations are obtained by taking a tenth, hundredth, thousandth, etc., of the unit chosen, and are designated by the Latin prefixes deci, centi, milli, etc., whilst the higher denominations are 10 times, 100 times, 1000, etc. times the unit, and are named by the Greek prefixes deca, hecto, kilo, etc.; examples of this will be found in the tables given below.

**561.** The starting-point of the French system is the "metre" (= 39.37 inches); this is the "unit of length." The "unit of measure" is the "litre," which is one cubic decimeter; the "unit of weight" is the gramme,<sup>1</sup> which is the weight of 1 cubic centimeter of distilled water at  $4^{\circ} C$ .

The chief conveniences arising from the use of this system are:

1st. That all the different denominations can be written as one, since they are either multiples by ten or are decimal fractions of the unit. Thus 5 decagrams, 3 grams, 4 decigrams, 8 milligrams, would be written 53.408 grams.

2d. That since 1 cubic centimeter of water at  $4^{\circ} C$ . weighs 1 gram we may obtain the *weight* of water to be used from the *measure* by simply converting the measure into cubic centimeters: the number thus obtained will represent at once the corresponding weight of water in grams. Of course this conversion is strictly accurate only when the water is measured at  $4^{\circ} C$ ., but for ordinary purposes the error introduced when the water is at the temperature of the air is too small to be of any importance in the preparation of solutions.

The weights and measures most frequently used for chemical purposes are the gram, the millimeter,<sup>2</sup> the liter, and the cubic centimeter,<sup>3</sup> which is  $\frac{1}{1000}$  of a liter.

### MEASURES OF LENGTH.

### ENGLISH.

	meter.	inches.	mile, furlong, yards, feet, inches.			
<sup>2</sup> Millimeter =	0.001 =	.03937 =				.03937
Centimeter =	0.01 =	.39371 =				.39371
Decimeter =	0.1 =	3.93708 =				3.9371
Meter =	1.0 =	39.37079 =			3	3.71
Decameter =	10.0 =	393.70790 =			10	2 9.7
Hectometer =	100.0 =	3937.07900 =			109	1 1
Kilometer =	1000.0 =	39370.79000 =			213	4 10.2
Myriometer =	10000.0 =	393707.90000 =	6	1	156	0 6

1 inch = .0254 meter.

1 foot = .3048 "

<sup>1</sup> Written "gram" in English, for the sake of brevity.

<sup>2</sup> Usually written (mm.).

<sup>3</sup> Usually abbreviated to (cc.).

## MEASURES OF CAPACITY.

1 liter = 4 cubic decimeters.

	liter.	cubic inches.	pints.
{ Milliliter, or Cubic centimeter (cc.) }	.001	.06103	0.00176
Centiliter	.01	.61027	0.01761
Deciliter	.1	6.1027	0.17608
Liter	1.0	61.027	1.76077
Decaliter	10.0	610.27	17.60773
Hectoliter	100.0	6102.7	176.07734
Kiloliter	1000.0	61027.0	1760.77341
Myrioliter	10000.0	610270.0	17607.73414

1 cubic inch = .01639 liter.

1 cubic foot = 28.31531 liters.

1 gallon = 4.54336 "

## MEASURES OF WEIGHT.

1 gram = the weight of 1 cubic centimeter (cc.) of water at 4° C.

	grams.	grains.	Avoirdupois.
Milligram	.001	0.01543	
Centigram	.01	0.15432	
Decigram	.1	1.54323	
Gram	1.0	15.43235	lbs. oz. drms.
Decagram	10.0	154.32349	= 0 0 5.65
Hectogram	100.0	1543.23488	= 0 3 8.5
Kilogram	1000.0	15432.34880	= 2 3 5
Myriogram	10000.0	154323.48800	= 22 1 2

1 grain = 0.0649 gram.

1 oz. (Troy) = 31.1035 grains.

1 lb. (Avoirdupois) = 453.593 "

## ENGLISH WEIGHTS AND MEASURES.

## APOTHECARIES WEIGHT.

lb.	oz.	drms.	scruples.	grains.
1	= 12	= 96	= 288	= 5760
	1	= 8	= 24	= 480
		1	= 3	= 60
			1	= 20

## AVOIRDUPOIS WEIGHT.

lb.	oz.	drms.	grains.
1	= 16	= 256	= 7000
	1	= 16	= 437.5
		1	= 27.343

## IMPERIAL MEASURE.

gallon.	pints.	fluid oz.	fluid drms.
1	= 8	= 160	= 1280
	1	= 20	= 160
		1	= 8

1 gallon = 70,000 grains of water at 16.7° C.

1 fluid ounce =  $\frac{1}{20}$  pint = 437.5 "

1 gallon = 277.280 cubic inches.

1 fluid ounce = 1.733 " "

# INDEX.

---

	PAGE
Acid, test for an, . . . . .	75
radicles, detection of, in simple substances, . . . . .	198, 205
"    "    detection of, in complex substances, . . . . .	242, 261
"    "    reactions of, . . . . .	147
Acids, removal from clothes, . . . . .	37
Acetates, reactions of, . . . . .	186
Acetic acid, . . . . .	186
Alkaline reaction, . . . . .	76
Alloys, . . . . .	278
Aluminium, reactions of, . . . . .	105
Ammonia gas, preparation of, . . . . .	34
"    "    properties of, . . . . .	35
"    "    tests for, . . . . .	36
Ammonium, reactions of, . . . . .	94
Analysis, course of, . . . . .	80
"    introduction to, . . . . .	82
"    of a simple liquid, . . . . .	196
"    "    solid, . . . . .	190
"    a complex liquid, . . . . .	233
"    "    solid, . . . . .	234
"    an alkaline liquid, . . . . .	200, 246
"    cyanogen compounds, . . . . .	288
"    insoluble substances, . . . . .	215, 283
"    metallic substances, . . . . .	214, 278
"    silicates, . . . . .	287
"    substances for, . . . . .	341
Analytical classification, . . . . .	83
"    "    table of, . . . . .	188
"    groups, . . . . .	84
"    reactions, . . . . .	91, 147
Antimony, reactions of, . . . . .	136
Apparatus, list of students', . . . . .	301
"    list of general, . . . . .	304
"    cleaning of, . . . . .	52
Arsenic group, . . . . .	128
"    "    separation and detection of, . . . . .	140
"    "    table of differences, . . . . .	140
Arsenic group, table for analysis, . . . . .	203, 253
"    reactions of, . . . . .	129
Atomic weights, list of, . . . . .	362

	PAGE
Barium group, . . . . .	101
“ “ separation and detection of, . . . . .	104
“ “ table of differences, . . . . .	103
“ “ table for analysis, . . . . .	205, 256
Barium, reactions*of, . . . . .	161
Bending glass tube, . . . . .	47
Beryllium, detection in analysis, . . . . .	355, 356
“ reactions of, . . . . .	350
Bismuth, reactions of, . . . . .	122
Blowpipe, use of, . . . . .	45, 69
Borates, reactions of, . . . . .	170
Borax bead, . . . . .	70
Boric acid, reactions of, . . . . .	171
Boring corks, . . . . .	47
Bromides, reactions of, . . . . .	161
Bunsen burner, . . . . .	43
Cadmium, reactions of, . . . . .	125
Cæsium, detection in analysis, . . . . .	355
“ reactions of, . . . . .	352
Calcium, reactions of, . . . . .	102
“ sulphate, preparation of, . . . . .	330
Carbon dioxide, preparation of, . . . . .	29
“ “ from combustion, . . . . .	33
“ “ from respiration, . . . . .	32
“ “ properties of, . . . . .	30, 32
“ “ tests for, . . . . .	32
“ “ in the air, . . . . .	33
Carbon monoxide, preparation of, . . . . .	37
“ “ properties of, . . . . .	38
“ “ tests for, . . . . .	39
Carbonates, reactions of, . . . . .	149
Carbonic acid, reactions of, . . . . .	150
Centigrade scale, . . . . .	362
Charcoal-wood, . . . . .	340
“ combustion in oxygen, . . . . .	34
“ ignition on, . . . . .	73
Chemicals, list for Section I, . . . . .	318
“ “ “ III, . . . . .	319
Chlorates, reactions of, . . . . .	157
Chloric acid, reactions of, . . . . .	158
Chloride group, separation and detection of, . . . . .	165
Chlorides, reactions of, . . . . .	158
Chlorine, preparation and properties of, . . . . .	39
“ tests for, . . . . .	39
“ water, preparation of, . . . . .	332
Chromium, reactions of, . . . . .	108
Chromates, reactions of, . . . . .	172
Classification of metals in groups, . . . . .	84
“ “ table of, . . . . .	188
Cleaning apparatus, . . . . .	52
“ platinum, . . . . .	53



	PAGE
Cobalt glass, . . . . .	304
"    reactions of, . . . . .	115
Combustion in oxygen, of charcoal, . . . . .	24
"    "    phosphorus, . . . . .	25
"    "    sulphur, . . . . .	24
Contractions, list of, . . . . .	84, 88
Copper group, separation and detection, . . . . .	125
"    "    table of differences, . . . . .	127
"    "    "    for analysis, . . . . .	203, 252
"    reactions of, . . . . .	123
Corks, . . . . .	340
"    boring of, . . . . .	47
Cutting glass tube, . . . . .	46
Cyanides, reactions of, . . . . .	178
Cyanogen compounds, analysis of, . . . . .	288
Decantation, process of, . . . . .	63
Detection of gold and platinum, . . . . .	281
Differences, table of; Group I, . . . . .	145
"    "    "    II A, . . . . .	127
"    "    "    II B, . . . . .	140
"    "    "    III A, . . . . .	109
"    "    "    III B, . . . . .	117
"    "    "    IV, . . . . .	103
"    "    "    V, . . . . .	97
Distillation of water, . . . . .	40, 301
"    nitric acid, . . . . .	42
Distilled water, tests for, . . . . .	41, 335
Drawing out glass tube, . . . . .	47
Drying precipitates, . . . . .	64
Elements, list of chemical, . . . . .	362
Entry in note-book, rules for, . . . . .	86
Entry of results, examples of, . . . . .	219, 293
Equation, chemical, . . . . .	87
Evaporation, process of, . . . . .	58
Fahrenheit scale, . . . . .	362
Ferricyanides, reactions of, . . . . .	181
Ferrocyanides, reactions of, . . . . .	180
Filter-paper, . . . . .	340
Filtration, process of, . . . . .	60
Flame colorations, . . . . .	71
Flask, tubulated, . . . . .	310
Fluorides, reactions of, . . . . .	174
Fluosilicates, reactions of, . . . . .	176
Fusion, process of, . . . . .	68
General table for groups, . . . . .	200, 246
"    "    detection of rarer elements, . . . . .	354

	PAGE
Glass tube, bending, . . . . .	47
“ “ cutting, . . . . .	46
“ “ drawing out, . . . . .	47
Gold, reactions of, . . . . .	146
“ detection of, . . . . .	251, 282
“ separation from platinum, . . . . .	282
Gram, . . . . .	364
Groups, analytical, . . . . .	84, 188, 189
Group III. precipitation and analysis of, . . . . .	209, 213-269
“ table for rarer elements, . . . . .	356
Heating glass and porcelain, . . . . .	55
Hydriodic acid, reactions of, . . . . .	164
Hydrobromic acid, . . . . .	162
Hydrochloric acid gas, preparation of, . . . . .	39
“ “ tests for, . . . . .	40
Hydrochloric acid, reactions of, . . . . .	160
Hydrocyanic acid, “ . . . . .	180
Hydrofluoric acid, “ . . . . .	176
Hydrofluosilic acid, “ . . . . .	178
“ “ preparation of, . . . . .	332
Hydrogen, collection of, . . . . .	26
“ combustion of, . . . . .	28
“ explosion of, . . . . .	29
“ preparation of, . . . . .	26
“ sulphide, reactions of, . . . . .	151
“ test for, . . . . .	29
Hydrosulphuric acid, reactions of, . . . . .	151
Hypochlorites, reactions of, . . . . .	103
Hypochlorous acid, reactions of, . . . . .	104
Hyposulphites, reactions of, . . . . .	152
Hyposulphurous acid, reactions of, . . . . .	153
Ignition, process of, . . . . .	67
“ on charcoal, . . . . .	73
Ignition-tubes, preparation of, . . . . .	49
Indigo-prism, . . . . .	304
Indium, detection in analysis, . . . . .	354, 356
“ reactions of, . . . . .	350
Insoluble substances, analysis of, . . . . .	215, 283
Iodides, reactions of, . . . . .	162
Iron group, . . . . .	105
“ separation and detection of, . . . . .	110
“ table of differences, . . . . .	109
“ table for analysis, . . . . .	254
Iron, reactions of, . . . . .	106
Labelling bottles, . . . . .	322
Labels, varnishing of, . . . . .	323
Lead, reactions of, . . . . .	121
Lime-water, preparation of, . . . . .	330

	PAGE
Liquid reagents, dilution of, . . . . .	316
Lithium, detection in analysis, . . . . .	355
"    reactions of, . . . . .	352
Litmus-paper, use of, . . . . .	75
Liter, the, . . . . .	364
 Magnesium, reactions of, . . . . .	95
Manganese, " . . . . .	112
Mercuricum, " . . . . .	119
Mercurous, " . . . . .	144
Metallic substances, analysis of, . . . . .	214, 278
Metals, examination for, . . . . .	200, 246
Molybdates, detection in analysis, . . . . .	354
"    reactions of, . . . . .	347
Mortar, agate, . . . . .	308
 Neutralizing, process of, . . . . .	77
Neutral reaction, . . . . .	75
Nickel, reactions of, . . . . .	113
Nitrates, " . . . . .	155
Nitric acid, reactions of, . . . . .	157
Nitric oxide, preparation of, . . . . .	34
Nitrites, reactions of, . . . . .	154
Nitrogen tetroxide solution, preparation of, . . . . .	333
Nitrous acid, reactions of, . . . . .	154
Notation, chemical, . . . . .	86
Notebook, rules for entry in, . . . . .	86
"    examples of entry, . . . . .	219, 293
 Organic acid-radicles, reactions of, . . . . .	178
Oxalates, reactions of, . . . . .	182
Oxalic acid, " . . . . .	183
Oxygen gas, collection of, . . . . .	22
"    "    experiments with, . . . . .	24, 25
"    "    preparation of, . . . . .	21
"    "    test for, . . . . .	25
 Palladium, detection in analysis of, . . . . .	354
"    reactions of, . . . . .	347
Phosphates, " " . . . . .	167
"    analysis of, . . . . .	212, 276
Phosphoric acid, reactions of, . . . . .	169
Phosphorus, combustion in oxygen, . . . . .	25
Platinum, detection of, . . . . .	282
"    reactions of, . . . . .	146
"    separation from gold, . . . . .	282
Platinum wire, mounting, . . . . .	51
"    "    cleaning, . . . . .	53
Potassium group, . . . . .	91
"    "    separation and detection, . . . . .	98

	PAGE
Potassium group, table of differences, . . . . .	97
“ “ table of analysis, . . . . .	100, 260
Potassium, reactions of, . . . . .	91
Precipitates, drying of, . . . . .	64
“ “ removal from filter, . . . . .	65
“ “ washing, . . . . .	63
Precipitation, process of, . . . . .	59
“ of Group III, remarks on, . . . . .	269
“ “ rules for, . . . . .	272
Preliminary examination for metals, . . . . .	192, 196, 236
“ “ for acid-radicles, . . . . .	198, 242
“ “ of cyanogen compounds, . . . . .	289
“ “ of insoluble substances, . . . . .	216, 284
“ “ of metallic substances, . . . . .	214, 278
Prussic acid, reactions of, . . . . .	180
Rarer elements, reactions of, . . . . .	345
“ “ tables for detection of, . . . . .	354, 356
Reactions, entry of, . . . . .	86
Reagents, addition of, in excess, . . . . .	229
“ preparation of, . . . . .	316
“ list of special, . . . . .	324
“ “ general, for metals, . . . . .	326
“ “ “ “ acid-radicles, . . . . .	328
Residues, silver, . . . . .	314
“ platinum, . . . . .	315
Rose burner, . . . . .	44
Rubidium, detection in analysis, . . . . .	355
“ reactions of, . . . . .	352
Rules for working, . . . . .	89
Saturated solutions, preparation of, . . . . .	330
Selenates, detection in analysis, . . . . .	354
“ reactions of, . . . . .	348
Selenites, “ . . . . .	348
Selenium, “ . . . . .	348
Silicates, analysis of, . . . . .	287
“ reactions of, . . . . .	173
Silicic acid, “ . . . . .	274
Silver group, . . . . .	143
“ “ separation and detection of, . . . . .	145
“ “ table of differences, . . . . .	145
“ “ table of analysis, . . . . .	251
“ reactions of, . . . . .	139
Simple substances, analysis of, . . . . .	187
Sodium, reactions of, . . . . .	95
Solubility, table of, . . . . .	266
Solution, process of, . . . . .	56
Solution of solid reagents, . . . . .	317
Solutions for reactions of metals, . . . . .	334
“ “ “ “ acid-radicles, . . . . .	336

	PAGE
Spectroscope, its use in analysis, . . . . .	358
Spectrum chart, . . . . .	361
Spirit-lamp, . . . . .	45
Steam-oven, . . . . .	308
Stirring-rods, preparation of, . . . . .	49
Strontium, reactions of, . . . . .	102
Sublimation, process of, . . . . .	68
Substances for analysis, . . . . .	341
Sulphates, reactions of, . . . . .	148
Sulphides, " . . . . .	151
Sulphites, " . . . . .	152
Sulphocyanides, reactions of, . . . . .	181
Sulphur, combustion in oxygen of, . . . . .	24
Sulphuretted hydrogen tube, . . . . .	48
"    "    apparatus, . . . . .	304
"    "    reactions of, . . . . .	151
"    "    passing . . . . .	307
"    "    solution, . . . . .	311
Sulphurous acid, reactions of, . . . . .	152
"    "    preparation of, . . . . .	331
Sulphuric acid, reactions of, . . . . .	148
Symbols, chemical, . . . . .	86
"    list of, . . . . .	362
Table for analysis of Group I, . . . . .	202, 251
"    "    II A, . . . . .	203, 252
"    "    II B, . . . . .	253
"    "    III A, . . . . .	204, 254
"    "    III B, . . . . .	204, 255
"    "    III A-B, . . . . .	209, 273, 274, 276
"    "    IV, . . . . .	205, 256
"    "    V, . . . . .	100, 258
"    "    phosphates, . . . . .	212, 276
Table of solubility, . . . . .	262
Tartaric acid, reactions of, . . . . .	185
Tartrates, reactions of, . . . . .	183
Tellurates, detection in analysis, . . . . .	354
"    reactions of, . . . . .	349
Tellurites, " . . . . .	348
Tellurium, " . . . . .	349
Test-papers, use of, . . . . .	75
Thallium, detection in analysis, . . . . .	354, 355, 356
"    reactions of, . . . . .	345
Theiosulphates, reactions of, . . . . .	152
Theiosulphuric acid, reactions of, . . . . .	153
Thermometric scales, conversion of, . . . . .	363
Tin, reactions of, . . . . .	138
Titanium, detection in analysis, . . . . .	355, 356
"    reactions of, . . . . .	350
Tungstates, detection in analysis, . . . . .	354
"    reactions of, . . . . .	346



	PAGE
Turmeric-paper, use of, . . . . .	78
Uranium, detection in analysis, . . . . .	355, 356
"    reactions of, . . . . .	349
Vanadium, detection in analysis, . . . . .	355
"    reactions of, . . . . .	351
Varnishing labels, . . . . .	323
Wash-bottle, . . . . .	50
Washing gases, . . . . .	37
"    precipitates, . . . . .	63
Water-bath, . . . . .	309
Water, distillation of, . . . . .	40, 311
"    distilling apparatus, . . . . .	311
Weights and measures, French and English, . . . . .	363, 364
Zinc group, . . . . .	110
"    "    separation and detection of, . . . . .	118
"    "    table of differences, . . . . .	117
"    "    "    for analysis, . . . . .	204, 256
Zinc, reactions of, . . . . .	111

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